Provided herein are electrolytes for lithium-ion electrochemical cells, electrochemical cells employing the electrolytes, methods of making the electrochemical cells and methods of using the electrochemical cells over a wide temperature range. Included are electrolyte compositions comprising a lithium salt, a cyclic carbonate, a non-cyclic carbonate, and a linear ester and optionally comprising one or more additives.

13 Claims, 42 Drawing Sheets
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* cited by examiner
Fig. 1

MCMB Carbon-LiNiCoO_2 Cells
25 mA Discharge current to 2.00 V
Temp = -40°C
MCMB Carbon-LiNiCoO₂ Cells
100 mA Discharge current to 2.00 V
Temp = -40°C

- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %)
- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 2% lithium oxalate
- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 2% VC
- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB

Fig. 2
Cycle Number

Discharge Capacity (Ah)

0.300
0.250
0.200
0.150
0.100
0.050
0.000

0 5 10 15 20 25 30 35 40

Cycling at 80°C
Cycling at 60°C

MCMB Carbon-LiNiCoO₂ Cells
50 mA Charge current to 4.10 V
50 mA Discharge current to 2.75 V
Temp = 60° and 80°C

- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %)
- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + lithium oxalate
- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 2% VC
- 1.2 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB

Fig. 3
MCMB Carbon-LiNiCoO₂ Cells

Lithium Reference Electrode

- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 2% FEC
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + lithium oxalate
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 2% VC
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 0.1M LiBOB

Temperature = 23°C

Fig. 4
Fig. 5

MCMB Carbon-LiNiCoO₂ Cells
Lithium Reference Electrode

Temperature = 23°C
MCMB Carbon-LiNiCoO₂ Cells
Lithium Reference Electrode

- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 2% FEC
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + lithium oxalate
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 2% VC
- 1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 0.10 M LiBOB

Temperature = -30°C

Fig. 6
Fig. 7

Graph showing the cathode potential (V vs L/Li) against current (Amps) with different electrolyte compositions:

- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 2% FEC
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + lithium oxalate
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 2% VC
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB

Temperature = -30°C
Li-ion Experimental Three Electrode Cell
MCMB Carbon - LiNi_{0.5}Co_{0.5}O_{2}
Lithium metal Reference Electrode

Temperature = 23°C

- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + lithium oxalate
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 2% VC
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB

Fig. 8
Li-ion Experimental Three Electrode Cell
MCMB Carbon - LINiCoO2
Lithium metal Reference Electrode

Temperature = 23°C

- Z' (Ohms)
- Z'' (Ohms)

1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %)
1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 4% FEC
1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + lithium oxalate
1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 2% VC
1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB

Fig. 9
Argonne National Lab. Electrodes
Graphite-LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ Cell
1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v/v %) Based Electrolytes
Temp = -40 °C

6.25 mA Discharge Current

- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v/v %)
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v/v %) + 4% FEC
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v/v %) + 2% lithium oxalate

Fig. 10
Argonne National Lab. Electrodes
Graphite-LiNi1/3Co1/3Mn1/3O₂ Cell
1.20 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) Based Electrolytes
Temp = -40 °C

12.5 mA Discharge Current

Fig. 11
Argonne National Lab. Electrodes
Graphite-LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cell
1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v/v) Based Electrolytes
Temp = -40 °C

25.0 mA Discharge Current

- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v/v)
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v/v) + 4% FEC
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v/v) + 2% lithium oxalate

Fig. 12
Argonne National Lab. Electrodes
Graphite-LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 Cell
1.20 M LiPF_6 EC+EMC+MB (20:20:60 v/v %) Based Electrolytes
Temp = -40 °C

41.7 mA Discharge Current

Fig. 13
Fig. 14

Li-ion Experimental Three Electrode Cell
Graphite-LiNi0.3Co0.3Mn0.4O2 Cell
Lithium metal Reference Electrode

Temperature = 23°C
Li-ion Experimental Three Electrode Cell
Graphite-LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} Cell
Lithium metal Reference Electrode

- 1.20 M LiPF\textsubscript{6} EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF\textsubscript{6} EC+EMC+MB (20:20:60 v/v %) + 4\% FEC
- 1.20 M LiPF\textsubscript{6} EC+EMC+MB (20:20:60 v/v %) + lithium oxalate

Temperature = 23°C

Fig. 15
Li-ion Experimental Three Electrode Cell
Graphite-LiNi0.5Co0.2Mn0.3O2 Cell
Lithium metal Reference Electrode

Temperature = - 20°C

- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + lithium oxalate

Fig. 16
Fig. 17

Li-ion Experimental Three Electrode Cell
Graphite-LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cell
Lithium metal Reference Electrode

Temperature = -20°C

- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %) + lithium oxalate
Fig. 18

- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + lithium oxalate

Lithium Experimental Three Electrode Cell
Graphite-LiNi0.5Co2.5Mn2O4 Cell
Lithium metal Reference Electrode

Temperature = -40°C

Current (Amps)

Cathode Potential (V vs Li+/Li)
Fig. 19

Li-Ion Experimental Three Electrode Cell
Graphite-LNi1/3Co1/3Mn1/3O2 Cell
Lithium metal Reference Electrode

Temperature = -40°C

- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF6 EC+EMC+MB (20:20:60 v/v %) + lithium oxalate

Anode Potential (mV vs Li+/Li)

Current (Amps)
Fig. 20
Li-ion Experimental Three Electrode Cell
Graphite-LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cell
Lithium metal Reference Electrode

Temperature = 23°C

Second Measurement
(After low temperature characterization testing)

- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %) + lithium oxalate

Current (Amps)

Fig. 21
Li-ion Experimental Three Electrode Cell
Graphite-LiNi$_{0.2}$Co$_{0.2}$Mn$_{0.6}$O$_2$ Cell
Lithium metal Reference Electrode

- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %)
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:50 v/v %) + 4% FEC
- 1.20 M LiPF$_6$ EC+EMC+MB (20:20:60 v/v %) + lithium oxalate

Temperature = 23°C

Fig. 22
Li-ion Experimental Three Electrode Cell
Graphite-LiNi<sub>1/3</sub>Co<sub>2/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> Cell
1.20M LiPF<sub>6</sub> in EC+EMC+MB (20:20:60 vol%) 
Lithium metal Reference Electrode

Anode Measurements
- Initial Measurement
- Prior to high temperature cycling
- After cycling at 60C

Fig. 23
Li-ion Experimental Three Electrode Cell
Graphite-LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cell
1.20M LiPF$_6$ in EC:EMC:MB (20:20:60 vol%) + 4% FEC
Lithium metal Reference Electrode

Anode Measurements

- Prior to high temperature cycling
- After cycling at 60°C
Li-ion Experimental Three Electrode Cell
Graphite-LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cell
1.20M LiPF$_6$ in EC+EMC+MB (20:20:60 vol%) + lithium oxalate
Lithium metal Reference Electrode

- Prior to high temperature cycling
- After cycling at 60C

Fig. 25
MCMB Carbon–LiNiCoAlO₂ Cells
25 mA Discharge current to 2.00 V
Temp = -30°C

Fig. 26
Fig. 27

MCMB Carbon–LiNiCoAlO₃ Cells
100 mA Discharge current to 2.00 V
Temp = -35°C

- 1.2 M LiPF₆ EC+EMC+MP (20:20:60 v/v%) (+ 4% FEC)
- 1.2 M LiPF₆ EC+EMC+MP (20:20:60 v/v%) + 2% lithium oxalate
- 1.2 M LiPF₆ EC+EMC+MP (20:20:60 v/v%) + 2% VC
- 1.2 M LiPF₆ EC+EMC+MP (20:20:60 v/v%) + 0.10M LiBOB
MCMB Carbon-LiNiCoO$_2$ Cell
50 mA Charge current to 4.10 V
50 mA Discharge current to 2.70 V
Temp = 60$^\circ$C

Discharge Capacity (Ah)

Cycle Number

Fig. 28
Fig. 29

MCM Carbon-C LiNiCoAlO₂ Cells
Lithium Reference Electrode

- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %)
- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + lithium oxalate
- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + 2% VC
- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + 0.10M LiBOB

Anode Potential (V vs Li⁺/Li⁺) vs Current (Amps)

Temperature = 23°C
**Fig. 30**

MCMB Carbon-LiNiCoAlO₂ Cells
Lithium Reference Electrode

Temperature = 23°C

- ▲ 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %)
- ♦ 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + 4% FEC
- □ 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + lithium oxalate
- ◆ 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + 2% VC
- ○ 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + 0.10M LiBOB
Fig. 31

MCMB Carbon-LiNiCoAlO$_2$ Cells
Lithium Reference Electrode

- 1.20 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %)
- 1.20 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %) + lithium oxalate
- 1.20 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %) + 2% VC
- 1.20 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %) + 0.10M LiBOB
Fig. 32

MCMB Carbon–LiNiCoO₂ Cells
Lithium Reference Electrode

Cathode Potential (V vs Li⁺/Li)

Temperature = -20°C

0.001 0.01 0.1 1
Current (Amps)

- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %)
- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + 4% FEC
- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + lithium oxalate
- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + 2% VC
- 1.20 M LiPF₆ EC+EMC+MP (20:20:60 v/v %) + 0.10M LiBOB
Lithium-Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2 Cell

1.2 M LiPF_6 EC+EMC+MP (20:20:60 v/v %) + 4% FEC
C/20 Charge current to 4.80 V
C/20 Discharge current to 2.00 V
Temp = 23°C

Charge Capacity = 3.478 mAh
Discharge Capacity = 2.781 mAh
Efficiency (1st Cycle) = 79.95%

Fig. 33
Lithium-Li[Li0.14Al0.86]Ni0.5Mn1.5O4, Cell
1.2 M LiPF6 EC:EMC:MP (20:20:60 v/v %) + 2% FEC
C/20 Charge current to 4.80 V
C/20 Discharge current to 2.00 V
Temp = 23°C

Discharge Capacity (mAh/g)

Cell JZ37

Fig. 34
Quallion MCMB-LiNiCoAlO₂ Lithium-Ion Cells
Quallion and JPL Low Temperature Electrolytes

C/10 Discharge Rate
Discharge Current = 0.025 A
Temperature = -60°C
C/5 Charge current to 4.1 V
Taper Cut-Off at ~C/100
Cells charged at 20°C

Fig. 35
Quallion MCMB-LiNiCoAlO₂ Lithium-Ion Cells
Quallion and JPL Low Temperature Electrolytes

C/2 Discharge Rate
Discharge Current = 0.125 A
Temperature = -60°C

C/5 Charge current to 4.1 V
Taper Cut-Off ~C/100
Cells charged at RT prior to LT discharge

Percent of Room Temperature Capacity (%)

Cell NEC-07-1.2M LiPF₆ EC+EMC (30:70)
Cell NA1-19 - Quallion Low Temperature Electrolyte "A1"
Cell NA2-35 - Quallion Low Temperature Electrolyte "A2"
Cell NA3-43 - Quallion Low Temperature Electrolyte "A3"
Cell NMP-08 - JPL Low Temperature Electrolyte (EC+EMC+MP)
Cell NEB-20 - JPL Low Temperature Electrolyte (EC+EMC+EB)

Fig. 36
Quallion MCMB-LiNiCoAlO₂ Lithium-Ion Cells
Quallion and JPL Low Temperature Electrolytes

2.0 C Discharge Rate
Temperature = -50°C
Discharge Current = 0.500 A

C/5 Charge current to 4.1 V
Taper Cut-Off at ~C/100
Cells charged at 20°C

A  Cell NEC-07-1.2M LiPF6 EC+EMC (30:70)
B  Cell NA1-19 - Quallion Low Temperature Electrolyte “A1”
C  Cell NA2-35 - Quallion Low Temperature Electrolyte “A2”
D  Cell NA3-43 - Quallion Low Temperature Electrolyte “A3”
E  Cell NMP-08 - JPL Low Temperature Electrolyte (EC+EMC+MP)
F  Cell NEB-20 - JPL Low Temperature Electrolyte (EC+EMC+EB)

Fig. 37
Quallion MCMB-LiNiCoAlO₂ Lithium-ion Cells
Quallion and JPL Low Temperature Electrolytes

4.0 C Discharge Rate
Discharge Current = 1.00 A
Temperature = -40°C

Fig. 38
Fig. 39

Quallion MCMB-LiNiCoAlO₂ Lithium-Ion Cell
Low Temperature Electrolyte (EC+EMC)
Cell NEC-09 (K08B604-09)

Temperature = ~40°C
C/5 Charge current to 4.1 V
Taper Cut-Off ~C/100
Cells charged at RT prior
to LT discharge

Cell Voltage (V)

Discharge Capacity (Ah)

- C/10 Discharge Rate (0.025 A)
- C/5 Discharge Rate (0.050 A)
- C/2 Discharge Rate (0.125 A)
- 1.0C Discharge Rate (0.250 A)
- 2.0C Discharge Rate (0.500 A)
- 3.0C Discharge Rate (0.750 A)
- 4.0C Discharge Rate (1.000 A)
- 5.0C Discharge Rate (1.250 A)
Quallion MCMB-LiNiCoAlO$_2$ Lithium-ion Cell
JPL Low Temperature Electrolyte (EC+EMC+MP)
Cell NMP-10 (K08C466-10)

Temperature = -40°C

C/5 Charge current to 4.1 V
Taper Cut-Off ~C/100
Cells charged at RT prior to LT discharge

Fig. 40
Quallion MCMB-LiNiCoAlO$_2$ Lithium-ion Cells
Quallion and JPL Low Temperature Electrolytes

Temperature = -40°C to +70°C

Discharge Capacity (Ah)

Cycle Number

Cell NEC-02 - Baseline Electrolyte (EC+EMC 30:70)
Cell NA1-18 - Quallion Electrolyte A1
Cell NA2-33 - Quallion Electrolyte A2
Cell NA3-42 - Quallion Electrolyte A3
Cell NMP-07 - JPL Low Temperature Electrolyte (EC+EMC+MP)
Cell NEB-19 - JPL Low Temperature Electrolyte (EC+EMC+EB)

25 mA Charge (C/10) to 4.10 V (at < -20°C)
50 mA Charge (C/5) to 4.10 V (at > 40°C)
C/50 Taper Current Cut-Off (0.005 A)
50 mA Discharge (C/5) to 2.5V

Fig. 41
125 mA Charge (C/2) to 2.70 V
C/50 Taper Cut-Off (0.005 A)
125 mA Discharge (C/2) to 1.20V
Temperature = -30°C to +40°C

Quallion Li$_3$Ti$_5$O$_{12}$-LiNiCoAlO$_2$
Lithium-Ion Cells

- Cell LEC-08 - Baseline Electrolyte (EC+EMC 30:70)
- Cell LEC-09 - Baseline Electrolyte (EC+EMC 30:70)
- Cell LA1-20 - Quallion Electrolyte A1
- Cell LA1-21 - Quallion Electrolyte A1
- Cell LMP-17 - JPL Low Temperature Electrolyte (EC+EMC+MP)

Fig. 42
ELECTROLYTES FOR WIDE OPERATING TEMPERATURE LITHIUM-ION CELLS

BACKGROUND

This invention is in the field of electrochemical devices, and relates generally to electrolytes for extending the operating temperature range of lithium-ion electrochemical cells. Electrolyte compositions, electrochemical cells employing the electrolyte compositions, and methods of making and using the electrochemical cells are provided.

A number of technical barriers associated with the development of Li-ion rechargeable batteries have been identified, including their narrow operating temperature range, limited life, and poor abuse tolerance. For this reason, there is an interest in the development of advanced electrolytes which will improve the performance of batteries over a wide range of temperatures (~30° to +40° C) and lead to long life characteristics (5,000 cycles over a 10-year life span). There is also interest in improving the high voltage stability of electrolyte systems to enable the operation of up to 5V with high specific energy cathode materials.

A number of future NASA missions and terrestrial applications, such as plug-in hybrid electric vehicles (PHEVs), require rechargeable batteries that can operate over a wide temperature range (~60 to +60° C) and provide good life characteristics. For example, future NASA missions aimed at exploring Mars and the outer planets will require rechargeable batteries that can operate at low temperatures to satisfy the requirements of various machinery, including landers, rovers, and penetrators. Currently, state-of-the-art lithium-ion systems demonstrate operability over a temperature range from ~30° C to +40° C; however, the rate capability at lower temperatures is poor due to poor electrolyte conductivity, poor lithium intercalation kinetics over the electrode surface layers, and poor ionic diffusion in the electrode bulk. In addition, the low temperature performance deteriorates rapidly once the cell has been exposed to high temperatures. However, improved rate capability of lithium-ion systems is desired at these very low temperatures (~30° to ~70° C), as well as good tolerance to warm temperatures.

Several factors can influence the low temperature performance of lithium-ion cells, including: (a) lithium ion mobility in the electrolyte solution (electrolyte conductivity), (b) interfacial characteristics (permittivity of ions through the solid electrolyte interphase layer, or "SEI" layer), (c) inherent properties of the electroactive materials (such as diffusion characteristics), and (d) cell design properties (such as electrode thickness, separator porosity, separator wetting properties, etc.). Of these parameters, the electrolyte-induced properties can be 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, it is desirable that the solvents possess a combination of several properties, such as: high dielectric constant, low viscosity, adequate coordination behavior, as well as appropriate liquid ranges and salt solubilities in the medium.

Reported all-carbonate based electrolyte compositions for lithium ion cells include an electrolyte formulation comprising LiPF₆ dissolved in a ternary, equi-proportion mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) (1:1:1 vol %); this electrolyte was demonstrated to provide long life over a wide temperature range (~30° to +40° C) (Smart et al., NASA Technical Report (NTR) NPO-20407 (Jan. 14, 1998) and U.S. Pat. No. 6,492,054). Further improvement of the low temperature performance (i.e., below ~30° C), was reported with a quaternary electrolyte formulation comprising 1.0 M LiPF₆, EC+DEC+DMC+EMC (1:1:1:2 v/v) (Smart et al., NTR NPO-20605 (Nov. 5, 1998)). Subsequent development led to the identification of a number of low EC-content ternary and quaternary solvent blend electrolytes, which have enabled excellent performance down to ~50° C (Smart et al., NTR NPO-30226 (Apr. 5, 2001)).

Low melting, low viscosity co-solvents have also been included in electrolyte mixtures. Smart et al., NTR NPO-19983 (Jul. 3, 1996) and NTR NPO-20601 (Oct. 28, 1998 have described the use of low viscosity and low melting point ester-based co-solvents, including methyl formate (MF), methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP), and ethyl butyrate (EB), in multi-component electrolyte formulations. The work reported in NTR NPO-19983 involved the following types of solutions: 0.50 M LiPF₆ in EC+DEC+methyl acetate (15:35:50 v/v/v), 0.50 M LiPF₆ in EC+DEC+methyl formate (15:35:50 v/v/v%), 0.50 M LiPF₆ in PC+DEC+methyl acetate (15:35:50 v/v/v%), 0.50 M LiPF₆ in PC+DEC+methyl formate (15:35:50 v/v/v%). The work reported in NTR NPO-20601 involved the following types of solutions: 1.00 M LiPF₆ in EC+DEC+DMC+ester (1:1:1:1 v/v/v/v%), where the ester=MA, EA, EP, or EB. Electrolytes were also investigated which incorporate large proportions of ester co-solvents (up to 80% by volume) which have been demonstrated to have excellent performance at very low temperatures, in a number of systems (M. C. Smart, B. V. Ratnakumar, A. Behar, L. D. Whitecanack, J.-S. Yu, M. Alamgir, "Gel Polymer Electrolyte Lithium-Ion Cells with Improved Low Temperature Performance", J. Power Sources, 165 (2), 535-543 (2007) and NPO-41097 (May 14, 2007). Smart et al., NTR NPO-41097 (May 14, 2007) have reported multi-component electrolytes of the following composition: 1.0 M LiPF₆ in ethylene carbonate (EC)-ethyl methyl carbonate (EMC)+X (1:1:8 v/v/v%) (where X=methyl butyrate (MB), ethyl butyrate (EB), methyl propionate (MP), and ethyl valerate (EV)). The performance of this latter group of electrolytes enabled performance down to very low temperatures (i.e., ~50 to ~70° C). Smart et al., J. Electrochem. Soc., 149(4), A361-A370 (2002) have reported that the higher molecular weight esters (e.g., ethyl propionate and ethyl butyrate) resulted in both improved low temperature performance and good stability at ambient temperatures. Excellent performance was obtained down to ~40° C with electrolytes comprising the following formulations: (a) 1.0 M LiPF₆
Although good performance was demonstrated at —20°C., its high reactivity toward the anode led to continued cell degradation and poor long term performance. Another group of electrolytes was developed in which the EC-content was fixed at 20% and the ester co-solvent at 20%. A number of ester co-solvents, namely methyl propionate (MP), ethyl propionate (EP), methyl butyrate (MB), ethyl butyrate (EB), propyl butyrate (PB), and butyl butyrate (BB), were included in multi-component electrolytes of the following composition: 1.0 M LiPF$_6$ in ethylene carbonate (EC) + methyl methyl carbonate (EMC) + X (20:60:20 v/v %) [where X=ester co-solvent] (Smart et al., NTR NPO-44974 (Mar. 9, 2001)). Other compositions reported include 1.20 M LiPF$_6$ in EC+EMC+MP (20:20:60 v/v %) and 1.20 M LiPF$_6$ in EC+DEC+EB (20:20:60 v/v %), which were demonstrated to operate well over a wide temperature range in MCMB-LiNiCoAlO$_2$ and Li$_x$Ti$_{2}$O$_{2}$-LiNiCoAlO$_2$ prototype cells. (Smart et al., NTR NPO-46976, Mar. 13, 2009) In other recent work, methyl butyrate-based electrolytes were demonstrated to have good performance in 2.2Ah LiFePO$_4$-based electrodes containing ethyl acetate (EA) and methyl butyrate (MB) have also been reported (Herreyre et al., J. Power Sources, 97-98, 576 (2001) and U.S. Pat. No. 6,399,255). More specifically, the following electrolyte formulations were reported: a) 1.0 M LiPF$_6$ in EC+DEC+MA (1:2:2), b) 1.5 M LiPF$_6$ in EC+DEC+MP (1:2:2), and c) 1.5 M LiPF$_6$ in EC+DEC+EP (1:2:2). Although promising performance was reported, the incorporation of a large proportion of diethyl carbonate (DEC) is not preferred due to the undesirable effects that this solvent has on the surface films of carbon anodes. Electrolytes containing ethyl acetate (EA) and methyl butyrate (MB) have also been reported (Herreyre et al., J. Power Sources, 97-98, 576 (2001) and U.S. Pat. No. 6,399,255). More specifically, the following electrolyte formulations were reported: a) 1.0 M LiPF$_6$ in EC+DEC+MA, b) 1.0 M LiPF$_6$ in EC+DEC+MB, c) 1.0 M LiPF$_6$ in EC+PC+MB, and d) 1.0 M LiPF$_6$ in EC+DEC+EA. Good low temperature performance with the methyl butyrate-based electrolyte was reported. Other researchers (Shiao et al., J. Power Sources, 87, 167-173 (2000)) have investigated the use of methacrylic acid and ethylene acetate in ternary mixtures with and without blending with toluene in an attempt to obtain improved performance to temperatures as low as —50°C. Other reports (Sazhin et al., J. Power Sources, 87, 112-117 (2000)) have involved the investigation of the performance of a number of electrolyte formulations at low temperatures, including the following: a) 1.0 M LiPF$_6$ in EC+EMC+EA (30:30:40), b) 1.0 M LiPF$_6$ in EC+DMC+MA (30:35:35), c) 1.0 M LiPF$_6$ in EC+DMC+EA (30:35:35), and d) 1.0 M LiPF$_6$ in EC+EMC+EP (30:30:40). Although good performance was demonstrated at —20°C, the performance attributes at temperatures below —20°C were not investigated.

Electrolyte additives have also been included in electrolyte compositions. Vinylene carbonate (VC) has been reported to be an effective additive in improving the high temperature cycle life and storage characteristics (G. G. Botte, R. E. White, and Z. Zhang, J. Power Sources, 97-98, 570 (2001); C. Jehoulet, P. Biensan, J. M. Bodet, M. Brussely, C. Moteau, C. Tessier-Lescourret, Proc. Electrochem. Soc. 97-18 (Batteries for Portable Electric Vehicles), The Electrochemical Society Inc., Pennington, N.J. (1997), pp. 974-985; D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, and U. Heider, Electrochim. Acta, 47 (9), 1423-1439 (2002)). It is generally held that VC sacrificially polymerizes on the electrode surfaces, producing protective films preventing further electrolyte reaction at the interface. Although the bulk of the studies have focused upon its effect during the formation process upon the SEI of the carbon electrode, it is acknowledged that it influences the nature of the films on the cathode also (M. C. Smart, B. L. Lucht, and B. V. Ratnakumar, “Electrochemical characteristics of MCMB and LiNi$_x$Co$_{1-x}$O$_2$ electrodes from cells containing electrolytes with stabilizing additives and exposed to high temperature”, J. Electrochem. Soc., 155, A557 (2008); M. Fujimoto, M. Takahashi, K. Nishio (Sanyo), U.S. Pat. No. 5,352,548, Oct. 4, 1994).


Lewis base electrolyte additives namely dimethyl aceta-mide (DMAC) and N-methylpyrroldinone (NMP) have been investigated as stabilizing agents (C.-H., Chen, Y. E. Hung, D. R. Vissers, and K. Amine., US Patent Application, 20030157413 (Aug. 21, 2003); C. L. Campion, W. Li, W. Euler, B. L. Lucht, B. Ravdel, J. DiCarlo, R. Gitzen, and M. A. Abraham, Electrochem. Solid-State Lett., 7, A194 (2004); C. L. Campion, W. Li and B. L. Lucht, J. Electrochem. Soc., 152, A2327 (2005); W. Li, C. L. Campion, B. L. Lucht, B. Ravdel, J. DiCarlo and K. M. Abraham, J. Electrochem. Soc., 152, A1361 (2005)). Good performance has been demonstrated for 1.0 M LiPF$_6$ in EC+DEC+DMC (1:1:1 v/v %) solutions with these additives after being subjected to high temperature storage (M. C. Smart, B. L. Lucht, and B. V. Ratnakumar, “The use of electrolyte additives to improve the high temperature resilience of Li-ion cells”, NTR NPO-44805 (Jan. 16, 2007); M. C. Smart, B. L. Lucht, and B. V. Ratnakumar, “Electrochemical characteristics of MCMB and LiNi$_x$Co$_{1-x}$O$_2$ electrodes from cells containing electrolytes with stabilizing additives and exposed to high temperature”, J. Electrochem. Soc., 155, A557 (2008)).

Mono-fluoroethylene carbonate has also been investigated in electrolyte solutions comprising FEC+EC+PC (1:3:3:5) primarily to prevent the exfoliation of graphite anode electrodes when used in the presence of propylene carbonate (PC) (R. McMullan, H. Siegl, Z. X. Shu, and W. Wang, J. Power Sources, 81-82: 20-26 (1999)). In a similar type of study, FEC was added to LiClO$_4$ dissolved in PC and the lithium deposition characteristics were investigated ((R. Mogi, M. Inaba, S.-K. Jeong, Y. Iriyama, T. Abe, and Z. Ogumi, J. Electrochem. Soc., 152, A2327 (2005); W. Li, C. L. Campion, B. L. Lucht, B. Ravdel, J. DiCarlo and K. M. Abraham, J. Electrochem. Soc., 152, A1361 (2005)). Good performance has been demonstrated for 1.0 M LiPF$_6$ in EC+DEC+DMC (1:1:1 v/v %) solutions with these additives after being subjected to high temperature storage (M. C. Smart, B. L. Lucht, and B. V. Ratnakumar, “The use of electrolyte additives to improve the high temperature resilience of Li-ion cells”, NTR NPO-44805 (Jan. 16, 2007); M. C. Smart, B. L. Lucht, and B. V. Ratnakumar, “Electrochemical characteristics of MCMB and LiNi$_x$Co$_{1-x}$O$_2$ electrodes from cells containing electrolytes with stabilizing additives and exposed to high temperature”, J. Electrochem. Soc., 155, A557 (2008)).

In one aspect, the present invention provides novel electrolyte compositions comprising a lithium salt, a cyclic carbonate, a non-cyclic carbonate, and a linear ester and optionally...
comprising one or more additives. The electrolytes of the present invention are useful in lithium ion electrochemical cells and can enable the electrochemical cells to operate over wide temperature ranges (e.g., —60° C. to +60° C.). These high performance electrolytes are capable of providing useful performance attributes when incorporated in electrochemical cells, such as specific capacities and rate capabilities higher than those of conventional state-of-the-art lithium-ion batteries. For example, the present invention provides electrolytes that can enable electrochemical cells capable of exhibiting cell voltages greater than or equal to 4.2 V. In addition, electrolytes of the present invention can enable electrochemical cells having a large cycle life and exhibiting good discharge stability upon cycling.

In another aspect, the present invention provides electrochemical cells including the electrolyte compositions of the invention. Lithium ion electrochemical cells of the invention are capable of good electrical power source performance over a wide temperature range (e.g., between —60° C. and +60° C.), high specific energies, useful discharge rate capabilities and good cycle life. Electrochemical cells of the present invention are versatile and include primary and secondary cells useful for a range of applications including use in extraterrestrial systems, military equipment and electric vehicles. Electrochemical cells of the present invention also can exhibit enhanced temperature tolerance relative to conventional state-of-the-art lithium-ion batteries. For example, electrolytes and electrochemical cells of the present invention extend the operating temperature of lithium-ion electrochemical cells to below —40° C.

In one aspect, the lithium ion electrochemical cells of the invention are capable of providing good electrical power performance at —60° C. In an embodiment, the cell provides a discharge energy of at least 20 Wh/kg, 40 Wh/kg or 60 Wh/kg at a discharge rate from C/5 to C/20 at —60° C. In another embodiment, the cell provides a discharge energy at room temperature (e.g. 23° C.) at a discharge rate from C/5 to C/20.

Also disclosed are methods of making electrochemical cells employing the electrolytes and methods of discharging the electrochemical cells. In an embodiment, the invention can provide a method of generating an electrical current wherein the cell provides a discharge energy of at least 20 Wh/kg, 40 Wh/kg or 60 Wh/kg at a discharge rate from C/5 to C/20 at —60° C. or provides at least 20%, 35%, or 50% of its discharge energy at room temperature (e.g. 23° C.) at a discharge rate from C/5 to C/20.

In an aspect, for example, provided is an electrolyte for use in an electrochemical cell, the electrolyte comprising a mixture of: 10-40% by volume cyclic carbonate; 10-50% by volume non-cyclic carbonate; 60% by volume linear ester; and a lithium salt may be selected from the group consisting of lithium hexafluorophosphate (LiPF₆), lithium tetrafluoroborate (LiBF₄), lithium bis(oxalato)borate (LiBOB), lithium difluoro(oxalato) borate (LiDFOB), and lithium hexafluoroarsenate (LiAsF₆), lithium perchlorate (LiClO₄), lithium trifluoromethanesulfonate (LiCF₃SO₃), lithium bis(bistrifluoromethanesulfonate sulfonyl imide (LiN(SO₂CF₃)₂)), lithium dinitramide (LiDNA) and combinations thereof. In one embodiment, the cyclic carbonate is ethylene carbonate (EC), the non-cyclic carbonate is ethyl methyl carbonate (EMC) and the linear ester is selected from: methyl propionate; ethyl propionate; methyl butyrate; ethyl butyrate; propyl butyrate; butyl butyrate; or a combination thereof.

In an aspect, for example, provided is an electrolyte for use in an electrochemical cell, the electrolyte comprising a mixture of: 10-40% by volume cyclic carbonate; 10-50% by volume non-cyclic carbonate; 20-80% by volume linear ester; and an additive selected from: mono-fluoroethylene carbonate (FEC); lithium oxalate; lithium bis(oxalato)borate (LiBOB); vinylene carbonate (VC); or a combination thereof. In another embodiment, the additive may be selected from mono-fluoroethylene carbonate (FEC); lithium oxalate; lithium bis(oxalato)borate (LiBOB); lithium difluoro(oxalato) borate (LiDFOB), lithium tetrafluoro(oxalato) phosphate (LiTFOP), vinylene carbonate (VC); vinylethylene carbonate (VEC or 4-vinyl-1,3-dioxolane-2-one) or a combination thereof.

In an aspect, for example, provided is an electrolyte for use in an electrochemical cell, the electrolyte comprising a mixture of: 10-40% by volume cyclic carbonate, wherein the cyclic carbonate is mono-fluoroethylene carbonate (FEC) or a combination of FEC and a non-fluorinated cyclic carbonate; 10-50% by volume non-cyclic carbonate; 20-80% by volume non-fluorinated linear ester; and a lithium salt in a concentration from —0.5M to 1.5M. In an embodiment, the lithium salt may be selected from lithium hexafluorophosphate (LiPF₆), lithium tetrafluoroborate (LiBF₄), lithium difluoro(oxalato) borate (LiDFOB), lithium tetrafluoro(oxalato) phosphate (LiTFOP), lithium hexafluoroarsenate (LiAsF₆), lithium perchlorate (LiClO₄), lithium trifluoromethanesulfonate (LiCF₃SO₃), lithium bis(bistrifluoromethanesulfonate sulfonyl imide (LiN(SO₂CF₃)₂)), lithium dinitramide (LiDNA) or combinations thereof. In an embodiment, the salt comprises LiPF₆. In an embodiment, the electrolyte further comprises an additive selected from: (i) lithium oxalate; (ii) lithium bis(oxalato)borate (LiBOB); (iii) vinylethylene carbonate (VC); or (vi) a combination of (i), (ii) and/or (iii).

In an aspect, for example, provided is an electrolyte for use in an electrochemical cell, the electrolyte comprising a mixture of: 10-40% by volume cyclic carbonate, wherein the cyclic carbonate is a non-fluorinated cyclic carbonate, mono-fluoroethylene carbonate (FEC) or a combination thereof; 10-50% by volume non-cyclic carbonate; 20-80% by volume linear ester; and a lithium salt in a concentration from —0.5M to 1.5M. In an embodiment, the lithium salt may be selected from lithium hexafluorophosphate (LiPF₆), lithium tetrafluoroborate (LiBF₄), lithium difluoro(oxalato) borate (LiDFOB), lithium tetrafluoro(oxalato) phosphate (LiTFOP), lithium hexafluoroarsenate (LiAsF₆), lithium perchlorate (LiClO₄), lithium trifluoromethanesulfonate (LiCF₃SO₃), lithium bis(bistrifluoromethanesulfonate sulfonyl imide (LiN(SO₂CF₃)₂)), lithium dinitramide (LiDNA) or combinations thereof; and lithium oxalate. In an embodiment, the lithium salt comprises LiPF₆. In an embodiment, the electrolyte further comprises an additive selected from: (i) lithium oxalate; (ii) lithium bis(oxalato)borate (LiBOB); (iii) vinylene carbonate (VC); or (vi) a combination of (i), (ii) and/or (iii).
combination of (i), and/or (ii). In an aspect, the cyclic carbonate, the non-cyclic carbonate and the linear ester are present in a combined total volume of 100 vol % and the lithium oxalate is present at a concentration between 0.5-3 vol % relative to the total volume.

In an aspect, for example, provided is an electrolyte for use in an electrochemical cell, the electrolyte comprising a mixture of: 10-40% by volume cyclic carbonate, wherein the cyclic carbonate is a non-fluorinated cyclic carbonate, mono-fluoroethylene carbonate (FE) or a combination thereof; 50-100% by volume non-cyclic carbonate; 20-80% by volume linear ester; a lithium salt in a concentration from ~0.5M to 1.5M. In an embodiment, the lithium salt may be selected from lithium hexafluorophosphate (LiPF₆), lithium tetrafluoroborate (LiBF₄), lithium difluoro(oxalato) borate (LiDFOB), lithium tetrafluoro(oxalato) phosphate (LiTPOP), lithium hexafluorosurolate (LiAsF₆), lithium perchlorate (LiClO₄), lithium trifluoromethanesulfonate (LiCF₃SO₃), lithium bis(trifluoromethanesulfonate) sulfonyl imide (LiNSO₂CF₃), lithium dinitramide (LiDNA) or combinations thereof. In an embodiment, the lithium salt comprises LiPF₆ and dimethyl carbonate (DMAC). In an embodiment, the electrolyte further comprises an additive selected from: (i) lithium oxalate; (ii) lithium bis(oxalato)borate (LiBOB); (iii) vinylene carbonate (VC); (iv) N-methylpyrrolidinone (NMP); or (v) a combination of (i), (ii), (iii) and/or (iv). In an aspect, the cyclic carbonate, the non-cyclic carbonate and the linear ester are present in a combined total volume of 100 vol % and the dimethyl carbonate (DMAC) is present at a concentration between 0.5-10 vol % or 0.5-3 vol % relative to the total volume.

In an aspect, for example, provided is an electrolyte for use in an electrochemical cell, the electrolyte comprising a mixture of: 10-40% by volume cyclic carbonate, wherein the cyclic carbonate is a non-fluorinated cyclic carbonate, mono-fluoroethylene carbonate (FE) or a combination thereof; 50-100% by volume non-cyclic carbonate; 20-80% by volume linear ester; a lithium salt in a concentration from ~0.5M to 1.5M. In an embodiment, the lithium salt may be selected from lithium hexafluorophosphate (LiPF₆), lithium tetrafluoroborate (LiBF₄), lithium difluoro(oxalato) borate (LiDFOB), lithium tetrafluoro(oxalato) phosphate (LiTPOP), lithium hexafluorosurolate (LiAsF₆), lithium perchlorate (LiClO₄), lithium trifluoromethanesulfonate (LiCF₃SO₃), lithium bis(trifluoromethanesulfonate) sulfonyl imide (LiNSO₂CF₃), lithium dinitramide (LiDNA) or combinations thereof. In an embodiment, the lithium salt comprises LiPF₆ and dimethyl carbonate (DMAC). In an embodiment, the electrolyte further comprises an additive selected from: (i) lithium oxalate; (ii) dimethyl carbonate (DMAC); (iii) vinylene carbonate (VC); (iv) N-methylpyrrolidinone (NMP); or (v) a combination of (i), (ii), (iii) and/or (iv). In an aspect, the LiBOB is present in a concentration of 0.5M to 1.5M. In an embodiment, the lithium salt may be selected from lithium hexafluorophosphate (LiPF₆), lithium tetrafluoroborate (LiBF₄), lithium difluoro(oxalato) borate (LiDFOB), lithium tetrafluoro(oxalato) phosphate (LiTPOP), lithium hexafluorosurolate (LiAsF₆), lithium perchlorate (LiClO₄), lithium trifluoromethanesulfonate (LiCF₃SO₃), lithium bis(trifluoromethanesulfonate) sulfonyl imide (LiNSO₂CF₃), lithium dinitramide (LiDNA) or combinations thereof; and lithium bis(oxalato)borate (LiBOB), wherein the electrolyte does not include a fluorinated ester. In an embodiment, the lithium salt comprises LiPF₆. In an embodiment, the electrolyte further comprises an additive selected from: (i) lithium oxalate; (ii) dimethyl carbonate (DMAC); (iii) vinylene carbonate (VC); (iv) N-methylpyrrolidinone (NMP); or (v) a combination of (i), (ii), (iii) and/or (iv). In an aspect, the LiBOB is present in a concentration of 0.05 M to 0.25 M.

In some embodiments, an electrolyte mixture comprises 15-30% by volume of the cyclic carbonate, 10-50% by volume of the non-cyclic carbonate, 40-70% by volume of the linear ester and, optionally, one or more additives. In one embodiment, an electrolyte mixture comprises 20% by volume of the cyclic carbonate, 20% by volume of the non-cyclic carbonate, 60% by volume of the linear ester and, optionally, one or more additives.

In some embodiments, for example, the non-fluorinated cyclic carbonate is ethylene carbonate (EC); the non-cyclic carbonate is selected from ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl propyl carbonate (MPC) or combinations thereof; the linear ester is a non-fluorinated linear ester; and/or the linear ester is selected from: (i) methyl propionate; (ii) ethyl propionate; (iii) methyl butyrate; (iv) ethyl butyrate; (v) propyl butyrate; (vi) butyl butyrate; or (vii) a combination of (i), (ii), (iii), (iv), (v) and/or (vi). In some embodiments, at least two linear esters are present, a first linear ester having a low viscosity and a second linear ester having a high viscosity.

In an aspect, for example, provided is a method of making an electrochemical cell comprising the steps of providing a cathode, providing an anode, and providing an electrolyte of the invention between the cathode and the anode. In an aspect, for example, an electrochemical cell comprises an anode, a cathode, and an electrolyte of the present invention provided between the anode and the cathode. Active materials for the electrodes of the electrochemical cells include lithium ion host materials capable of accommodating lithium ions from the electrolyte during discharge and charging of the electrochemical cells. In this context, accommodation of lithium ions includes insertion of lithium ions into the host material, intercalation of lithium ions into the host material and/or reaction of lithium ions with the host material. Accommodation includes alloy formation reactions, surface reaction and/or bulk reactions with the host material. Use of lithium ion host materials that are capable of reversibly exchanging lithium ions with the electrolyte without significant degradation of the lithium ion host material upon cycling is preferred for secondary lithium ion batteries of the present invention. In some embodiments, the cathode comprises a material selected from LiCoO₂, LiMn₂O₄, LiMPO₄ (M=Fe, Co, Mn), LiNiCoAlO₂, LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂, LiNiCo₀.₃₃Co₀.₃₃Mn₀.₃₃O₂, LiNi₀.₅Co₀.₅O₂, LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂, LiNi₀.₅Mn₁.₅O₄ or LiNi₀.₃₃Co₀.₃₃Ni₀.₃₃Mn₀.₃₃O₂. In some embodiments, the anode comprises a carbon-based material or a material selected from natural graphite, synthetic graphite, hard carbon, mesocarbon microbeads (MCMB), silicon-carbon composites, lithium titanate (Li₄Ti₅O₁₂), lithium metal and combinations thereof. The carbon-based material may be a pure or doped carbonaceous material, and may be amorphous, semi-crystalline, crystalline, or a mixture thereof. In some embodiments, electrochemical cells of the invention have standard cell voltages equal to or greater than 4.3 V. In some embodiments, cathodes may be charged to potentials of 4.6V to 4.8V. In such high voltage cells, the anode may be carbon-based and the cathode may be selected from a layered-layered composite LiNiCoMnO₂, LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ or LiNi₀.₃₃Co₀.₃₃Ni₀.₃₃Mn₀.₃₃O₂. In some embodiments, electrochemical cells of the invention operate at temperatures between ~20° C. and ~60° C.

Cathodes operating at high potentials may benefit from the presence of electrolyte additives that lead to protective surface layers on the cathode (especially LiBOB). Due to the presence of fluorination, electrolytes that possess FEC may also have inherently greater electrochemical stability at high potentials. Thus, the use of FEC and LiBOB in conjunction may provide desirable effects with high voltage systems.

In an aspect, for example, provided is an electrochemical cell comprising an anode devoid of an electrochemically active carbon compound; a cathode comprising a material selected from the group consisting of LiCoO₂, LiMn₂O₄, LiMPO₄ (M=Fe, Co, Mn), LiNiCoAlO₂, LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂, LiNiCo₀.₃₃Co₀.₃₃Mn₀.₃₃O₂, LiNi₀.₅Co₀.₅O₂, LiNi₀.₅Mn₁.₅O₄ and LiNi₀.₃₃Mn₀.₃₃O₂; and an electrolyte provided between the anode and the cathode, the electrolyte comprising a mixture of: 15-30% by volume of a saturated cyclic carbonate selected from the group consisting of ethylene
carbonate (EC), mono-fluoroethylene carbonate (FEC) and combinations thereof; 10-50% by volume of a non-cyclic carbonate selected from the group consisting of ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl propyl carbonate (MPC) and combinations thereof; 40-70% by volume linear ester selected from the group consisting of: (i) methyl propionate; (ii) ethyl propionate; (iii) methyl butyrate; (iv) ethyl butyrate; (v) propyl butyrate; (vi) butyl butyrate; and (vii) a combination of (i), (ii), (iii), (iv), (v) and/or (vi); a lithium salt in a concentration from 0.8 M to 1.4 M, the lithium salt selected from the group consisting of lithium hexafluorophosphate (LiPF₆), lithium bis(oxalato) borate (LiBOB), lithium difluoro(oxalato) borate (LiDFOB), lithium tetrafluoroborate (LiBF₄), lithium trihexylphosphate (LiTFOP), lithium bis(trifluoromethanesulfonfyl)imide (LiTFSI), lithium trifluoromethanesulfonate (LiCF₃SO₃), lithium bis(trifluoromethanesulfonfyl)imide (Li[N(SO₂CF₃)₂]), lithium dimethyl carbonate (LiDMC) and combinations thereof; and 0.5-5% or 1.5-2.5% by volume vinylene carbonate.

Electrochemical cells of these aspects are useful generally for extraterrestrial and vehicle applications that require batteries to be discharged, and optionally charged, under challenging temperature conditions (e.g., between -60°C and +60°C). In an aspect, for example, provided is a method of generating an electrical current, the method comprising the steps of providing an electrochemical cell containing an anode, a cathode, and an electrolyte of the present invention provided between the anode and the cathode, the cell being in a charged state; and discharging the electrochemical cell.

A variety of compounds are useful as the additive component(s) of the present electrolytes, including but not limited to: mono-fluoroethylene carbonate (FEC); lithium oxalate, lithium bis(oxalato)borate (LiBOB); lithium difluoro(oxalato) borate (LiDFOB), lithium tetrafluoro(oxalato) phosphate (LiTFOP), vinylene carbonate (VC); vinylethylene carbonate (VEC or 4-vinyl-1,3-dioxolane-2-one) and combinations thereof. In other embodiments, dimethyl carbonate (DMC) and/or N-methylpyrrolidinone (NMP) may be included in the electrolyte composition. Additives can be useful for suppressing, or eliminating, degradation of electrochemical cell components (e.g., electrodes). In some embodiments, for example, the additive itself may chemically decompose on an electrode surface to form a protective solid electrolyte interphase (SEI). According to this aspect, therefore, the additive functions as a sequestering agent. Additives in electrolytes of the present invention can be useful for: (i) producing desirable, protective solid electrolyte interphase (SEI) layers on the electrode surfaces (anode and/or cathode); (ii) enhancing the lithium kinetics at the interface regions of the electrodes; (iii) sequestering reactive decomposition species; and (iv) providing enhanced safety.

As discussed above, the mechanisms by which the various additives impart a beneficial effect upon cell performance can differ. In the inventive electrolyte compositions described herein, experimental results indicate that VC and FEC can contribute to SEI formation. VEC is also expected to contribute to film formation. LiBOB is believed to participate in film formation at both electrodes and can be especially beneficial at the cathode, but also functions as an electrolyte salt contributing to the ionic conductivity of the media. Lithium difluoro(oxalato) borate (LiDFOB) and lithium tetrafluoro(oxalato) phosphate (LiTFOP), which are related in structure to LiBOB, are expected to function similarly. Lithium oxalate is believed to complex any deleterious PF₅ that may be generated due to the decomposition of LiPF₆ (either thermally or by contact with water), and may participate in formation of desirable surface films. Dimethyl carbonate (DMC) and/or N-methylpyrrolidinone (NMP) would also be expected to function as complexing agents. Based on the different mechanisms of providing desirable effects, mixtures of additives may be especially beneficial.

In the present work, it was found that in some situations additives improved the performance of the electrochemical cells at temperatures above room temperature (vs. similar electrochemical cells without additives). An unintended benefit to the low temperature discharge rate capability was observed with the use of several electrolyte additives, resulting in greater discharge capacity and operating voltage (i.e., reduced polarization effects). It was ascertained that this was due to increased lithium kinetics at the electrodes, due to the formation of desirable surface films (especially at the cathode, which is most often the limiting electrode). This enhancement was observed to be system dependent (i.e., for LiNiCoO₂ the following trend was observed: LiBOB>VC>lithium oxalate>FEC; whereas for LiNi-CoAlOₓ the trend was: VC>FEC>lithium oxalate>LiBOB). Based on these results, it is believed that combinations of additives may further improve the enhanced kinetics since the benefit manifested itself differently at anode and cathode (i.e., LiBOB and VC enhanced the kinetics at the cathode, whereas FEC and lithium oxalate enhanced the kinetics at the anode). It was also observed that some electrolyte additives led to better performance than others if charging at high rates at low temperatures is required of the cell (i.e., to avoid the possibility of lithium plating which degrades life). VC and LiBOB were identified as being undesirable due to observed lithium plating with high rate, low temperature charging, whereas FEC and lithium oxalate were more desired.

The concentrations and physical properties of the additives are important parameters for supporting a range of electrochemical cell functionalities. In some embodiments, the additive is present in a concentration less than or equal to 40 vol %, and optionally in some embodiments less than or equal to 20 vol %, and optionally in some embodiments less than or equal to 10 vol %, and optionally in some embodiments less than or equal to 5 vol %, and optionally in some embodiments less than or equal to 2.5 vol %.

The concentrations and physical properties of the additives are important parameters for supporting a range of electrochemical cell functionalities. In some embodiments, the additive is present in a concentration less than or equal to 40 vol %, and optionally in some embodiments less than or equal to 20 vol %, and optionally in some embodiments less than or equal to 10 vol %, and optionally in some embodiments less than or equal to 5 vol %, and optionally in some embodiments less than or equal to 2.5 vol %.

The concentrations and physical properties of the additives are important parameters for supporting a range of electrochemical cell functionalities. In some embodiments, the additive is present in a concentration less than or equal to 40 vol %, and optionally in some embodiments less than or equal to 20 vol %, and optionally in some embodiments less than or equal to 10 vol %, and optionally in some embodiments less than or equal to 5 vol %, and optionally in some embodiments less than or equal to 2.5 vol %.
performed after the cells were subjected to high temperature based electrolytes at —40° C. using a C/4 discharge rate.

The measurements were performed after the cells were subjected to high temperature cycling (60° C. and 80° C.).

FIG. 4 shows Tafel polarization measurement of MCMB electrodes from MCMB-LiNiCoO₂ cells containing various methyl butyrate-based electrolytes at 25° C.

FIG. 5 shows Tafel polarization measurement of LiNiCoO₂ electrodes from MCMB-LiNiCoO₂ cells containing various methyl butyrate-based electrolytes at 25° C.

FIG. 6 shows Tafel polarization measurement of MCMB electrodes from MCMB-LiNiCoO₂ cells containing various methyl butyrate-based electrolytes at —30° C.

FIG. 7 shows Tafel polarization measurement of LiNiCoO₂ electrodes from MCMB-LiNiCoO₂ cells containing various methyl butyrate-based electrolytes at —30° C.

FIG. 8 shows EIS measurements performed on MCMB electrodes from MCMB-LiNiCoO₂ cells containing various methyl butyrate-based electrolytes. The measurements were performed after the cells were subjected to high temperature cycling (60-80° C.).

FIG. 9 shows EIS measurements performed on LiNiCoO₂ electrodes from MCMB-LiNiCoO₂ cells containing various methyl butyrate-based electrolytes. The measurements were performed after the cells were subjected to high temperature cycling (60-80° C.).

FIG. 10 shows discharge characteristics at —40° C. and 6.25 mA of cells containing methyl butyrate-based electrolytes.

FIG. 11 shows discharge characteristics at —40° C. and 12.5 mA of cells containing methyl butyrate-based electrolytes.

FIG. 12 shows discharge characteristics at —40° C. and 25.0 mA of cells containing methyl butyrate-based electrolytes.

FIG. 13 shows discharge characteristics at —40° C. and 41.7 mA of cells containing methyl butyrate-based electrolytes.

FIG. 14 shows Tafel polarization measurements of cells containing methyl butyrate-based electrolytes.

FIG. 15 shows Tafel polarization measurements of cells containing methyl butyrate-based electrolytes.

FIG. 16 shows Tafel polarization measurements of cells containing methyl butyrate-based electrolytes at —20° C.

FIG. 17 shows Tafel polarization measurements of cells containing methyl butyrate-based electrolytes at —20° C.

FIG. 18 shows Tafel polarization measurements of cells containing methyl butyrate-based electrolytes at —40° C.

FIG. 19 shows Tafel polarization measurements of cells containing methyl butyrate-based electrolytes at —40° C.

FIG. 20 shows a comparison of the Tafel polarization measurements of the anode and cathode at different temperatures for a cell containing methyl butyrate-based electrolyte including 4% FEC.

FIG. 21 shows Tafel polarization measurements of cells containing methyl butyrate-based electrolytes.

FIG. 22 shows Tafel polarization measurements of cells containing methyl butyrate-based electrolytes.

FIG. 23 shows anode EIS measurements of a cell containing a reference electrolyte composition after high temperature cycling.

FIG. 24 shows anode EIS measurements of a cell containing a methyl butyrate-based electrolyte composition after high temperature cycling.

FIG. 25 shows EIS measurements of an anode containing a methyl butyrate-based electrolyte composition after high temperature cycling.

FIG. 26 shows the discharge capacity (Ah) of MCMB-LiNiCoAlO₂ lithium-ion cells containing various methyl propionate-based electrolytes at —30° C. using a C/5 discharge rate.

FIG. 27 shows the discharge capacity (Ah) of MCMB-LiNiCoAlO₂ lithium-ion cells containing various methyl propionate-based electrolytes at —30° C.

FIG. 28 shows the cycling characteristics of experimental MCMB-LiNiCoAlO₂ lithium-ion cells containing various methyl propionate-based electrolytes at high temperatures (60° C.).

FIG. 29 shows Tafel polarization measurement of MCMB electrodes from MCMB-LiNiCoAlO₂ cells containing various methyl propionate-based electrolytes.

FIG. 30 shows Tafel polarization measurement of LiNiCoAlO₂ electrodes from MCMB-LiNiCoAlO₂ cells containing various methyl propionate-based electrolytes.

FIG. 31 shows Tafel polarization measurement of MCMB electrodes from MCMB-LiNiCoAlO₂ cells containing various methyl propionate-based electrolytes.

FIG. 32 shows Tafel polarization measurement of LiNiCoAlO₂ electrodes from MCMB-LiNiCoAlO₂ cells containing various methyl propionate-based electrolytes.

FIG. 33 shows the discharge and charge capacity of a Li—Li(Li₀·₁₇Ni₀·₂₅Mn₀·₅₈)₀·₃₀O₂ cell containing a methyl propionate-based electrolyte with a mono-fluoroethylene carbonate (FEC) additive.

FIG. 34 shows the discharge capacity of Li(Li₀·₁₂Ni₀·₂₅Mn₀·₅₈)₀·₃₀O₂ electrodes from Li—Li(Li₀·₁₂Ni₀·₂₅Mn₀·₅₈)₀·₃₀O₂ cells containing a methyl propionate-based electrolyte with a mono-fluoroethylene carbonate (FEC) additive.

FIG. 35 shows the discharge capacity (Ah) of Quallion MCMB-LiNiCoAlO₂ Li-ion cells, containing various low temperature electrolytes, when discharged at —60° C. using a C/10 rate (cells charged at room temperature).

FIG. 36 shows the discharge capacity (Ah) of Quallion MCMB-LiNiCoAlO₂ Li-ion cells, containing various low temperature electrolytes, when discharged at —60° C. using a C/2 rate (cells charged at room temperature).

FIG. 37 shows the discharge capacity (Ah) of Quallion MCMB-LiNiCoAlO₂ Li-ion cells, containing various low temperature electrolytes, when discharged at —50° C. using a 2.0 C rate (cells charged at room temperature).

FIG. 38 shows the discharge capacity (Ah) of Quallion MCMB-LiNiCoAlO₂ Li-ion cells, containing various low temperature electrolytes, when discharged at —40° C. using a 4.0 C rate (cells charged at room temperature).

FIG. 39 shows the discharge capacity (Ah) of Quallion MCMB-LiNiCoAlO₂ Li-ion cells, containing the baseline all-carbonate electrolyte, when discharged at —40° C. using various rates (cells charged at room temperature).

FIG. 40 shows the discharge capacity (Ah) of Quallion MCMB-LiNiCoAlO₂ Li-ion cells, containing the methyl propionate-based electrolyte, when discharged at —40° C. using various rates (cells charged at room temperature).
DETAILED DESCRIPTION OF THE INVENTION

In general, the terms and phrases used herein have their art-recognized meaning, which can be found by reference to standard texts, journal references and contexts known to those skilled in the art. The following definitions are provided to clarify their specific use in the context of the invention.

“Standard electrode potential” (E°) refers to the electrode potential when concentrations of solutes are 1 M, gas pressures are 1 atm and the temperature is 25 degrees Celsius. As used herein standard electrode potentials are measured relative to a standard hydrogen electrode.

“Electrode potential” refers to a voltage, usually measured against a reference electrode, due to the presence of chemical species at different oxidation (valence) states within or in contact with the electrode.

“Electrolyte” refers to an ionic conductor which can be in solid, liquid state and/or gas (e.g., plasma).

“Additive”, as used herein, refers to a compound or combination of compounds that acts as a sacrificial agent or a sequestering agent to improve performance of an electrochemical cell. Typically, additives serve to increase conductivity of an electrolyte and/or protect one or more electrode materials from substantial degradation.

“Cation” refers to a positively charged ion, and “anion” refers to a negatively charged ion.

“Viscosity” refers to a liquid's resistance to flow.

Electrolytes of the present invention have the general formula: Li-salt+cyclic carbonate+non-cyclic carbonate+linear ester. In one particular embodiment, electrolytes of the present invention have the formula: Li-salt+EC and/or FEC+EMC+linear ester, where the linear ester is MP, MB and/or EB.

Cyclic carbonates useful for the present invention include non-fluorinated carbonates, fluorinated carbonates, and combinations thereof. Useful non-fluorinated carbonates include ethylene carbonate (EC). Useful fluorinated carbonates include mono-fluoroethylene carbonate (FEC).

Non-cyclic carbonates useful for the present invention include asymmetric alkyl carbonates. In an embodiment, the asymmetric alkyl carbonate is ethyl methyl carbonate (EMC). In another embodiment, non-cyclic carbonate may be ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl propyl carbonate (MPC) or combinations thereof.

Linear esters useful in the present invention include alkyl esters. In an embodiment, the alkyl ester has the general formula R'COOR", where R' and R" are, independently, C₁₋₁₀ aliphatic, especially C₃₋₁₀ alkyl, including branched, straight chain, and cycloaliphatic. In an embodiment, R' and R" are, independently, C₃₋₁₀ alkyl, especially C₃₋₄ alkyl. In an embodiment, the linear ester is selected from: methyl propionate (MP); ethyl propionate (EP); methyl butyrate (MB); ethyl butyrate (EB); propyl butyrate (PB); butyl butyrate (BB); or a combination thereof. In an embodiment, the linear ester is a “low viscosity ester” having a relatively low viscosity. The low viscosity ester has a low molecular weight, which can contribute to good mobility and high conductivity, especially at low temperatures. In an embodiment, a low viscosity ester displays a viscosity less than 0.70 cP at 25° C. Suitable low viscosity esters include, but are not limited to, methyl propionate and methyl butyrate.

In another embodiment, linear ester is a “high viscosity ester” having a relatively high viscosity and molecular weight. In an embodiment, the high molecular weight esters display viscosities greater than 0.70 cP at 25° C. and boiling points >110° C. The high viscosity ester possesses a higher boiling point and lower vapor pressure than the low viscosity ester, thereby providing enhanced resilience to high temperatures. Suitable high viscosity esters include, but are not limited to, propyl butyrate and butyl butyrate. In one embodiment an electrolyte comprises two esters, a low viscosity ester and a high viscosity ester. In different embodiments, the proportions (by volume) of the high and low viscosity esters may be 50:50, 25:75 to 75:25 or 10:90 to 90:10. For higher temperature applications, it may be preferred to use a greater proportion of the high viscosity ester.
In the present work, MP-based electrolytes were observed to provide higher rate capability (especially at lower temperatures), whereas MB-based electrolytes provided somewhat higher temperature resilience. The high temperature resilience and life characteristics (both cycle and calendar life) are further enhanced by the addition of electrolyte additives, where the desired additive can vary depending upon electrode couple (most notably the cathode material). In general, both MP-based and MB-based electrolytes work well with LiNiCoAlO$_2$, LiNiCoO$_2$, LiCoO$_2$, LiMn$_2$O$_4$, and LiIMPO$_4$-based systems.

Lithium salts may both impart conductivity and contribute to solid electrode interphase (SEI) layer formation. In an embodiment, the lithium salt may be selected from the group consisting of lithium hexafluorophosphate (LiPF$_6$), lithium tetrafluoroborate (LiBF$_4$), lithium bis(oxalato)borate (Li$_2$B$_4$O$_7$), lithium difluoro(oxalato) borate (LiFDOB), lithium tetrafluoro(oxalato) phosphate (LiTFOF), lithium hexafluorornasenate (LiAsF$_6$), lithium perchlorate (LiClO$_4$), lithium trifluoromethanesulfonate lithium trifluoromethanesulfonate sulfonyl imide (LiNiSO$_4$CF$_3$$_2$), lithium dinitramide (LiDNA) and combinations thereof. In an embodiment, the lithium salt comprises LiPF$_6$. In an embodiment, the electrolyte may contain a first lithium salt which is present in relatively high concentration and a second lithium salt which is present in relatively low concentration. In an embodiment, this second lithium salt may be viewed as an additive. In an embodiment, the additive salt may be selected from lithium bis(oxalato)borate (Li$_2$B$_4$O$_7$); lithium difluoro(oxalato) borate (LiFDOB), lithium tetrafluoro(oxalato) phosphate (LiTFOF), or combinations thereof.

Electrolyte components for the present electrolytes were selected based on a number of selection criteria. For example, components of the present electrolytes display a high conductivity, e.g., 1 mS cm$^{-1}$ from -60 to 40$^\circ$ C, and low melting point, e.g., -60 to 75$^\circ$ C, so that the components remain conductive and liquid over a wide temperature range. Components of the present electrolytes are also good for good electrochemical stability over a wide voltage window, e.g., 0 to 4.5 V, good chemical and thermal stability, good compatibility with the chosen electrode couple, good SEI characteristics on the electrode, facile lithium intercalation/de-intercalation kinetics, low inflammability, and low toxicity. Tables 1-4 show exemplary electrolyte components and concentrations, electrolyte compositions and ratios, additive combinations, and electrode and electrolyte combinations.

**TABLE 1** Exemplary electrolyte components and concentration ranges.

<table>
<thead>
<tr>
<th>Component</th>
<th>Broader Range</th>
<th>Narrower Range(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Salt</td>
<td>0.3M-1.5M</td>
<td>0.8M-1.25M</td>
</tr>
<tr>
<td>Lithium hexafluorophosphate (LiPF$_6$)</td>
<td>0.5M-1.4M</td>
<td>0.8M-1.2M</td>
</tr>
<tr>
<td>Lithium bis(oxalato)borate (Li$_2$B$_4$O$_7$)</td>
<td>0M-0.25M</td>
<td>0.05M-0.25M</td>
</tr>
<tr>
<td>Lithium tetrafluoroborate (LiBF$_4$)</td>
<td>0M-0.25M</td>
<td>0.05M-0.25M</td>
</tr>
<tr>
<td>Lithium difluoro(oxalato) borate (LiFDOB)</td>
<td>0M-0.25M</td>
<td>0.1M-0.15M</td>
</tr>
<tr>
<td>Lithium tetrafluoro(oxalato) phosphate (LiTFOF)</td>
<td>0M-0.25M</td>
<td>0.05M-0.25M</td>
</tr>
<tr>
<td>Lithium dinitramide (LiDNA)</td>
<td>0M-0.25M</td>
<td>0.05M-0.25M</td>
</tr>
<tr>
<td>Cyclic Carbonate</td>
<td>10 vol %-40 vol %</td>
<td>15 vol %-30 vol %</td>
</tr>
<tr>
<td>Ethylene carbonate (EC)</td>
<td>0 vol %-40 vol %</td>
<td>0 vol %-25 vol %</td>
</tr>
<tr>
<td>Methyl propylene carbonate (MEC)</td>
<td>0 vol %-40 vol %</td>
<td>1 vol %-40 vol %</td>
</tr>
<tr>
<td>Non-Cyclic Carbonate</td>
<td>10 vol %-50 vol %</td>
<td>15 vol %-30 vol %</td>
</tr>
</tbody>
</table>

**TABLE 2** Exemplary electrolyte compositions and ratios.

<table>
<thead>
<tr>
<th>Electrolyte Compositions</th>
<th>Ratio (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC:EMC</td>
<td>20:20:60</td>
</tr>
<tr>
<td>EC:EMC:M</td>
<td>20:20:60</td>
</tr>
<tr>
<td>EC:EMC:B</td>
<td>20:20:60</td>
</tr>
<tr>
<td>EC:EC:EMC</td>
<td>10:10:60</td>
</tr>
<tr>
<td>EC:EC:EMC:MP</td>
<td>20:20:60</td>
</tr>
</tbody>
</table>

**TABLE 3** Exemplary additive combinations.

<table>
<thead>
<tr>
<th>Additive Combinations</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>V:LiBOB</td>
<td>F:EC:LiBOB</td>
</tr>
<tr>
<td>LiNiO$_2$: graphite</td>
<td>F:EC:LiBOB</td>
</tr>
<tr>
<td>LiCoO$_2$: graphite</td>
<td>F:EC:C</td>
</tr>
</tbody>
</table>

**TABLE 4** Exemplary electrode and electrolyte combinations.

<table>
<thead>
<tr>
<th>Cathode/Anode</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMPO$_4$</td>
<td>EC:EMC:M (20:20:60 vol %) + 4% FEC</td>
</tr>
<tr>
<td>LiNiCoAlO$_2$</td>
<td>EC:EMC:M (20:20:60 vol %) + 2% VC</td>
</tr>
<tr>
<td>M = Fe, Co, Mn</td>
<td>1.2M LiPF$_6$ EC:EMC:M (20:20:60 vol %)</td>
</tr>
<tr>
<td>LiNiCoAlO$_2$: graphite</td>
<td>1.2M LiPF$_6$ EC:EMC:M (20:20:60 vol %)</td>
</tr>
<tr>
<td>LiCoO$_2$: graphite</td>
<td>1.2M LiPF$_6$ EC:EMC:M (20:20:60 vol %) + 4% FEC</td>
</tr>
<tr>
<td>LiPF$_6$</td>
<td>1.2M LiPF$_6$ EC:EMC:M (20:20:60 vol %) + 2% VC</td>
</tr>
<tr>
<td>LiMPO$_4$</td>
<td>1.2M LiPF$_6$ EC:EMC:M (20:20:60 vol %) + 0.1M LiBOB</td>
</tr>
<tr>
<td></td>
<td>1.2M LiPF$_6$ EC:EMC:M (20:20:60 vol %) + lithium oxide</td>
</tr>
</tbody>
</table>
Methyl Butyrate-Based Electrolyte Solutions Containing Additives MCMB-LiNiCoO₂ Cells

In the current study, we demonstrated improved performance of Li-ion cells with methyl butyrate-based electrolytes, including:

1. 1.0 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 4% FEC
2. 1.0 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + lithium oxalate
3. 1.4 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 4% FEC
4. 1.0 M LiPF₆ EC+EMC+MB (20:20:60 v/v %) + 2% VC

Lithium-ion cells, comprising MCMB carbon anodes and LiNi₀.₅Mn₀.₅O₂ cathodes, were utilized to study the electrolytes. These cells served to verify and demonstrate the reversibility, low temperature performance, and electrochemical aspects of each electrode as determined from a number of electrochemical characterization techniques.

Formation Characteristics

As illustrated in Table 5, good performance characteristics of the cells containing the methyl butyrate-based electrolytes with and without the use of electrolyte additives were observed, as judged from the coulombic efficiency on the first cycle (being an indication of the inherent stability and the electrode film forming process) and the cumulative irreversible capacity losses. As displayed, the cell containing the mono-fluoroethylene carbonate as an additive was observed to have notably low irreversible capacity loss over the first five cycles and much higher coulombic efficiency on the first cycle. These results suggest that very desirable solid electrolyte interphase (SEI) layers are being formed on the electrode (especially on the carbon anode).

TABLE 5

<table>
<thead>
<tr>
<th>Electrolyte Type</th>
<th>Charge Capacity (Ah)</th>
<th>Discharge Capacity (Ah)</th>
<th>Irreversible Capacity (1st Cycle)</th>
<th>Coulombic Efficiency (1st Cycle)</th>
<th>Charge Capacity (Ah)</th>
<th>Reversible Capacity (5th Cycle)</th>
<th>Cumulative Irreversible Capacity (1st-5th Cycle)</th>
<th>Coulombic Efficiency (5th Cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2M LiPF₆ EC + EMС + MB (20:20:60 v/v %)</td>
<td>0.4791</td>
<td>0.4071</td>
<td>0.072</td>
<td>84.96</td>
<td>0.4104</td>
<td>0.3973</td>
<td>0.1326</td>
<td>96.80</td>
</tr>
<tr>
<td>1.2M LiPF₆ EC + EMС + MB (20:20:60 v/v %) + 4% FEC</td>
<td>0.4619</td>
<td>0.3998</td>
<td>0.062</td>
<td>86.55</td>
<td>0.3831</td>
<td>0.3825</td>
<td>0.0726</td>
<td>99.83</td>
</tr>
<tr>
<td>1.2M LiPF₆ EC + EMС + MB (20:20:60 v/v %) + lithium oxalate</td>
<td>0.4571</td>
<td>0.3935</td>
<td>0.064</td>
<td>86.10</td>
<td>0.3927</td>
<td>0.3850</td>
<td>0.1011</td>
<td>98.05</td>
</tr>
<tr>
<td>1.2M LiPF₆ EC + EMС + MB (20:20:60 v/v %) + 2% VC</td>
<td>0.4711</td>
<td>0.3938</td>
<td>0.077</td>
<td>83.59</td>
<td>0.3939</td>
<td>0.3868</td>
<td>0.1153</td>
<td>98.20</td>
</tr>
<tr>
<td>1.2M LiPF₆ EC + EMС + MB (20:20:60 v/v %) + 0.10M LiBOB</td>
<td>0.3856</td>
<td>0.3196</td>
<td>0.066</td>
<td>82.87</td>
<td>0.4054</td>
<td>0.3969</td>
<td>0.1123</td>
<td>97.92</td>
</tr>
</tbody>
</table>
Discharge Characteristics

After performing the formation cycling, the cells were subjected to systematic discharge rate characterization testing over a wide temperature range. These tests included charging the cells at ambient temperature and then soaking the cells for at least four hours prior to discharging at the desired temperatures. The results of these studies are summarized in Table 6.

Since the rationale of adding the electrolyte additives was to improve the high temperature resilience, it is significant that the discharge rate capability is somewhat comparable for all of the formulations investigated. This suggests that the electrolyte additives are not having a negative impact upon the cell impedance, limiting the low temperature performance. For example, as displayed in FIG. 1, when the cells were discharged at -C/16 discharge rate at -40° C. very comparable performance of the electrolyte without any additives (the baseline formulation) and those with additives was obtained, with approximately 75% of the room temperature capacity being delivered.

In contrast, in many cases the cells containing the electrolyte additives actually deliver better performance than the baseline formulation (i.e., the performance characteristics of the anode and cathode may degrade at different rates depending upon the electrolyte type).

Electrochemical Characteristics

It is believed that the improved rate capability at low temperatures of Li-ion cells that utilized these ester-based solutions is primarily due to improved mass transfer characteristics in the electrolyte (higher ionic conductivity) and facile kinetics of lithium intercalation/de-intercalation at the interface due to favorable film formation behavior at the electrode surfaces. To enhance this understanding, as well as the impact that the electrolyte additives have upon these factors, we assessed the electrochemical characteristics of the systems using a number of techniques, including Tafel polarization measurements, Electrochemical Impedance Spectroscopy (EIS), and linear micro-polarization measurements.

To determine the lithiation/de-lithiation kinetics of the anodes and the cathodes of the various systems, Tafel polarization measurements of the MCMB-LiNi1/2Co1/2O2 cells were performed. The measurements were conducted on the cells while they were in a full state of charge (SOC) (OCV = 4.07 V) before and after each storage period. In all of these Tafel plots, there are distinct charge-transfer controlled regimes, where the overpotential increases linearly with log (I). The effect of mass transfer seems to be relatively insign-
significant which allows one to obtain kinetic parameters, such as the exchange current and the transfer coefficients. As illustrated in FIG. 4, with the exception of the cell containing LiBOB, improved lithium de-intercalation kinetics (i.e., higher limiting currents) were observed for the anodes in contact with the electrolytes possessing the electrolyte additives compared to the baseline formulation, suggesting that a desirable surface film has formed in these cases.

As illustrated in FIG. 5, in which the Tafel polarization measurements have been performed on the LiNiCoO₂ cathodes at room temperature, the cell containing the VC and lithium oxalate electrolyte additives displayed enhanced lithium kinetics (i.e., higher limiting current densities) compared to the baseline formulation. This observation, namely that VC has a beneficial effect upon the nature of the SEI layer, has been observed in our previous studies involving different LiBOB, improved lithium de-intercalation kinetics (i.e., higher limiting currents) were observed for the anodes in contact with the electrolytes possessing the electrolyte additives compared to the baseline formulation, suggesting that a desirable surface film has formed in these cases.

As illustrated in FIG. 6, the cells containing the VC and lithium oxalate additives displayed enhanced lithium kinetics (i.e., higher limiting currents) were observed for the anodes in contact with the electrolytes possessing the electrolyte additives compared to the baseline formulation, suggesting that a desirable surface film has formed in these cases.

As illustrated in FIG. 7, a different trend was observed compared to that displayed at 20° C.; FIGS. 14 through 19 show initial Tafel polarization measurements for the cathode and anode of graphite-LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ experimental Li-ion cells (cell chemistry developed by Argonne National Lab). The electrolytes selected for evaluation included: (1) 1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %), (2) 1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %)+4% FEC, and (3) 1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %)+lithium oxalate.

As illustrated in Table 7, good performance was obtained with these electrolytes over a wide temperature range.

### Table 7

<table>
<thead>
<tr>
<th>Current (mA) Rate</th>
<th>Capacity (Ah)</th>
<th>Percent (%)</th>
<th>Capacity (Ah)</th>
<th>Percent (%)</th>
<th>Capacity (Ah)</th>
<th>Percent (%)</th>
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<td>25.0 mA</td>
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<td>0.11486</td>
<td>100.00</td>
<td>0.10794</td>
<td>100.00</td>
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<td></td>
</tr>
<tr>
<td>6.25 C/16</td>
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<td>0.09486</td>
<td>82.59</td>
<td>0.09734</td>
<td>90.18</td>
</tr>
<tr>
<td>8.33 C/12</td>
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<td>67.49</td>
<td>0.09237</td>
<td>80.42</td>
<td>0.09607</td>
<td>89.00</td>
</tr>
<tr>
<td>12.50 C/8</td>
<td>0.06533</td>
<td>61.31</td>
<td>0.08757</td>
<td>76.24</td>
<td>0.09984</td>
<td>84.16</td>
</tr>
<tr>
<td>25.00 C/4</td>
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<td>0.08334</td>
<td>72.56</td>
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<tr>
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<td>0.07851</td>
<td>68.35</td>
<td>0.07684</td>
<td>72.80</td>
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<td>0.07379</td>
<td>62.28</td>
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<td>0.06611</td>
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<td>56.94</td>
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<tr>
<td>41.67 C/2</td>
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<td>51.19</td>
<td>0.07379</td>
<td>62.28</td>
<td>0.06930</td>
<td>64.21</td>
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<td>-50° C.</td>
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<td></td>
</tr>
<tr>
<td>6.25 C/16</td>
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<td>0.06311</td>
<td>54.95</td>
<td>0.04852</td>
<td>44.69</td>
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<tr>
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<td>0.06107</td>
<td>53.17</td>
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<tr>
<td>12.50 C/8</td>
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<td>47.33</td>
<td>0.04157</td>
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<td>25.00 C/4</td>
<td>0.00766</td>
<td>7.19</td>
<td>0.03567</td>
<td>31.06</td>
<td>0.02348</td>
<td>21.75</td>
</tr>
<tr>
<td>41.67 C/2</td>
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<td>0.00796</td>
<td>6.93</td>
<td>0.00555</td>
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<td>-60° C.</td>
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<td></td>
</tr>
<tr>
<td>6.25 C/16</td>
<td>0.00827</td>
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<td>0.02832</td>
<td>22.91</td>
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<td>11.81</td>
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<td>8.33 C/12</td>
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<td>0.00878</td>
<td>7.65</td>
<td>0.00141</td>
<td>1.07</td>
</tr>
<tr>
<td>12.50 C/8</td>
<td>0.00162</td>
<td>1.52</td>
<td>0.00315</td>
<td>2.74</td>
<td>0.00792</td>
<td>7.33</td>
</tr>
</tbody>
</table>

TABLE 7

Summary of the discharge characteristics of graphite - LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ cells containing various electrolytes over a wide temperature range (−60 to +23° C.). Cells were charged at 20° C.

Graphite LiNi₁.₃₃Co₁.₃₃Mn₁.₃₃O₂ Cells

In addition to evaluating the technology in MCMB-LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ cells, selected electrolytes were also evaluated in graphite-LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ experimental Li-ion cells (cell chemistry developed by Argonne National Lab). The electrolytes selected for evaluation included: (1) 1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %), (2) 1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %)+4% FEC, and (3) 1.20M LiPF₆ in EC+EMC+MB (20:20:60 v/v %)+lithium oxalate.

As displayed in Table 7, the incorporation of the electrolyte additives, namely mono-fluoroethylene carbonate and lithium oxalate, further improved the low temperature capabilities over the baseline formulation. It should also be noted that all of these formulations dramatically outperform state-of-the-art all-carbonate based electrolytes under these conditions.

FIGS. 10 through 13 show discharge characteristics of graphite-LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ cells containing the MB-based electrolyte at −40° C. using a discharge current of 6.25 mA, 12.5 mA, 25 mA and 41.7 mA, respectively.

FIGS. 14 through 19 show initial Tafel polarization measurements for the cathode and anode of graphite-LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ cells containing various MB-based electrolytes.

As displayed in Table 7, the incorporation of the electrolyte additives, namely mono-fluoroethylene carbonate and lithium oxalate, further improved the low temperature capabilities over the baseline formulation. It should also be noted that all of these formulations dramatically outperform state-of-the-art all-carbonate based electrolytes under these conditions.

FIGS. 10 through 13 show discharge characteristics of graphite-LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ cells containing the MB-based electrolyte at −40° C. using a discharge current of 6.25 mA, 12.5 mA, 25 mA and 41.7 mA, respectively.

FIGS. 14 through 19 show initial Tafel polarization measurements for the cathode and anode of graphite-LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ cells containing various MB-based electrolytes.
temperature with respect to the cathode. In addition, the baseline formulation performed better in both MB-based electrolytes at the anode (graphite) at room temperature, and this trend holds at approximately -20°C. At -40°C, however, both the FEC and lithium oxalate MB-based electrolytes perform better than the baseline formulation at the anode, but both are outperformed by the baseline formulation at the cathode.

FIG. 20 compares Tafel polarization measurements at different temperatures for an electrolyte containing 4% FEC. FIGS. 21 and 22 show room temperature Tafel polarization measurements following methyl butyrate electrolyte characterization. The MB-based electrolyte containing the lithium oxalate additive continued to perform either the FEC or baseline formulation at room temperature, but the baseline formulation displayed much lower limiting current densities and this trend holds at -20°C. At -10°C, a C/5 rate, the following methyl butyrate-based solutions containing the lithium oxalate additive continued to outperform both the FEC and lithium oxalate systems at low temperatures, protecting the nature of the SEI at the anode. The performance of the electrolytes containing additives was similar both before and after high temperature cycling. Thus, the use of mono-fluorooxyethylene carbonate (FEC) and lithium oxalate have been shown to improve the performance (both at low and high temperature) when incorporated into methyl butyrate-based electrolytes with the LiNi0.5Co0.2Mn0.3O2 system.

LiFePO4-Based Cells

In addition to the FEC and lithium oxalate systems discussed above, we have demonstrated good cycle life and improved low temperature of LiFePO4-based cells using the following methyl butyrate-based electrolytes:
1) 1.2M LiPF6 EC+EMC+MB (20:20:60)+4% FEC
2) 2M LiPF6 EC+EMC+MB (20:20:60)+2% VC

As shown in Table 8, these systems were capable of supporting >11 C discharge rates at ~30°C, with over 90% of the room temperature capacity being delivered. The cells also performed well down to ~-60°C, with 80% of the room temperature capacity being delivered using a C/10 rate. Good cycle life performance was observed up to 50°C, and the cells displayed resilience to variable temperature cycling (i.e., charging and discharging at low temperature as well as high). Cells were A123 2.20 Ah cells.

<table>
<thead>
<tr>
<th>Temp</th>
<th>Rate</th>
<th>Ah</th>
<th>Wh</th>
<th>Wh/kg</th>
</tr>
</thead>
<tbody>
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<td>20°C C/5</td>
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<td>2.242</td>
<td>7.284</td>
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<td>35.04</td>
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<td>2.278</td>
<td>6.738</td>
<td>94.64</td>
</tr>
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</table>

A. Summary of the discharge characteristics of LiFePO4-based cells containing various electrolytes. Temperature Range 20° C to -10° C; Cells were discharged to 1.50V.
### Table 8-continued

#### Summary of the discharge characteristics of LiFePO₄-based cells containing various electrolytes.

**Temperature Range** -20°C to -50°C; Cells were discharged to 0.50 V

<table>
<thead>
<tr>
<th>Temp</th>
<th>Rate</th>
<th>Cells</th>
<th>Baseline Electrolyte</th>
<th>Baseline Electrolyte (20:20:60 v/v %)</th>
<th>Baseline Electrolyte + 4% FEC (20:20:60 v/v %)</th>
</tr>
</thead>
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</table>

### Table 9

#### Summary of the discharge characteristics of LiFePO₄-based cells containing various electrolytes.

**Temperature Range** -50°C to -20°C; Cells were discharged to 0.50 V

<table>
<thead>
<tr>
<th>Temp</th>
<th>Rate</th>
<th>Cells</th>
<th>Baseline Electrolyte</th>
<th>Baseline Electrolyte (20:20:60 v/v %)</th>
<th>Baseline Electrolyte + 4% FEC (20:20:60 v/v %)</th>
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</table>

### Table 10

#### Summary of the discharge characteristics of LiFePO₄-based cells containing various electrolytes.

**Temperature Range** 20°C to 60°C; Cells were discharged to 0.50 V

<table>
<thead>
<tr>
<th>Temp</th>
<th>Rate</th>
<th>Cells</th>
<th>Baseline Electrolyte</th>
<th>Baseline Electrolyte (20:20:60 v/v %)</th>
<th>Baseline Electrolyte + 4% FEC (20:20:60 v/v %)</th>
</tr>
</thead>
<tbody>
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<td>US 9,293,773 B2</td>
<td>US 9,293,773 B2</td>
</tr>
</tbody>
</table>
Although modestly higher capacity fade rates were observed with the MB-based electrolytes compared with the LiNiCoAlO$_2$ cathodes, good resilience to low temperature charging was also observed with no apparent lithium plating.

Example 2

Methyl Propionate-Based Electrolyte Solutions Containing Additives

In the current study, we demonstrated improved performance of Li-ion cells with methyl propionate-based electrolytes, including:

1. 1.0 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %) +4% FEC
2. 1.0 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %) +2% FEC
3. 1.4 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %) +lithium oxalate
4. 1.0 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %) +2% VC
5. 1.0 M LiPF$_6$ EC+EMC+MP (20:20:60 v/v %) +0.10M LiBOB

Discharge Characteristics

After performing the formation cycling, the cells were subjected to systematic discharge rate characterization testing over a wide temperature range. These tests included charging the cells at ambient temperature and then soaking the cells for at least four hours prior to discharging at the desired temperatures. The results of these studies are summarized in Table 10.
electrolyte additives was to improve the high temperature resilience, it is significant that the discharge rate capability was significantly improved for many of the formulations investigated. For example, as displayed in FIG. 26, when the cells were discharged at -30°C discharge rate at -30°C. All of the cells containing the electrolyte additives were observed to outperform the baseline methyl propionate blend, with the formulations containing VC and FEC yielding the best performance.

This trend was also observed when the cells were evaluated at higher rates at low temperature. As shown in FIG. 27, when the cells were evaluated using a 100 mA discharge current (corresponding to a -0.8 C rate) at -30°C, a similar trend was observed compared with that at the lower rate. Again, the cells containing the VC and FEC additives outperformed the baseline solution most dramatically. These results suggest that the lithium intercalation/de-intercalation kinetics are more favorable with the cells containing the electrolyte additives, presumably due to preferable SEI formation characteristics. In order to decipher the influence of the electrolyte additives upon the kinetics of the respective electrodes, detailed electrochemical characterization of the cells was performed, as described below.

After performing the rate characterization testing, a cycling test was performed on the cells at high temperature to determine their high temperature resilience. This included performing 20 cycles at 60°C, followed by electrochemical characterization. As illustrated in FIG. 28, the cells containing the LiBOB and FEC additives displayed the best initial capacity and capacity retention after being subjected to cycling at 60°C. One of the major objectives of performing the electrochemical characterization upon completing the cycling at high temperature was to determine the manner in which the various additives influenced the degradation rates at both the anodes and the cathodes.

Electrochemical Characteristics

It is believed that the improved rate capability at low temperatures of Li-ion cells that utilized these ester-based solutions is primarily due to improved mass transfer characteristics in the electrolyte (higher ionic conductivity) and facile kinetics of lithium intercalation/de-intercalation at the interface due to favorable film formation behavior at the electrode surfaces. To enhance this understanding, as well as the impact that the electrolyte additives have upon these factors, we have assessed the electrochemical characteristics of the systems using a number of techniques, including Tafel polarization measurements, Electrochemical Impedance Spectroscopy (EIS), and linear micro-polarization measurements.

To determine the lithiation/de-lithiation kinetics of the anodes and the cathodes of the various systems, Tafel polarization measurements of the MCMB-LiNiCoAlO2 cells were performed. The measurements were conducted on the cells while they were in a full state of charge (SOC) (OCV=4.07V) before and after each storage period. In all of these Tafel plots, there are distinct charge-transfer controlled regimes, where the overpotential increases linearly with log (i). The effect of mass transfer seems to be relatively insignificant which allows one to obtain kinetic parameters, such as the exchange current and the transfer coefficients. As illustrated in FIG. 29, improved lithium de-intercalation kinetics (i.e., higher limiting currents) were observed for the anodes in contact with the electrolytes possessing the FEC, and to a lesser extent the VC, electrolyte additives compared to the baseline formulation, suggesting that a desirable surface film has formed in these cases.

As illustrated in FIG. 30, in which the Tafel polarization measurements have been performed on the LiNiCoAlO2 cathodes at room temperature, all of the cells containing electrolyte additives appeared to display enhanced lithium kinetics (i.e., higher limiting current densities) compared to the baseline formulation. It was observed that the addition of LiBOB had the most beneficial effect upon the nature of the SEI layer on the cathode and the corresponding lithium kinetics.

Generally, the trends with regard to the observed lithium kinetics and how they depend upon electrolyte type tend to track well with temperature. For example, when Tafel measurements were performed on the MCMB anodes at low temperature, as displayed in FIG. 31, the cells containing the FEC were again observed to deliver improved performance over the baseline formulation. In addition, when the LiNiCoAlO2 cathodes were measured at -20°C, as shown in FIG. 32, a similar trend was observed compared to that displayed at 20°C, with the cell containing the LiBOB delivering the best performance.

---

**TABLE 10-continued**

Summary of the discharge characteristics of MCMB-LiNiCoAlO2 cells containing various electrolytes over a wide temperature range (-50 to +23°C). Cells were charged at 20°C.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Current (mA)</th>
<th>Capacity (Ahr)</th>
<th>Percent (%)</th>
<th>Capacity (Ahr)</th>
<th>Percent (%)</th>
<th>Capacity (Ahr)</th>
<th>Percent (%)</th>
<th>Capacity (Ahr)</th>
<th>Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30°C</td>
<td>25 mA</td>
<td>0.0617</td>
<td>51.09</td>
<td>0.0891</td>
<td>66.95</td>
<td>0.0860</td>
<td>66.87</td>
<td>0.0964</td>
<td>74.82</td>
</tr>
<tr>
<td>-30°C</td>
<td>50 mA</td>
<td>0.0544</td>
<td>44.99</td>
<td>0.0872</td>
<td>65.57</td>
<td>0.0745</td>
<td>61.83</td>
<td>0.0917</td>
<td>71.14</td>
</tr>
<tr>
<td>-30°C</td>
<td>100 mA</td>
<td>0.0466</td>
<td>38.33</td>
<td>0.0801</td>
<td>60.25</td>
<td>0.0691</td>
<td>57.32</td>
<td>0.0858</td>
<td>66.62</td>
</tr>
<tr>
<td>-40°C</td>
<td>25 mA</td>
<td>0.0413</td>
<td>34.20</td>
<td>0.0773</td>
<td>58.12</td>
<td>0.0660</td>
<td>54.77</td>
<td>0.0833</td>
<td>64.62</td>
</tr>
<tr>
<td>-40°C</td>
<td>50 mA</td>
<td>0.0356</td>
<td>29.46</td>
<td>0.0729</td>
<td>54.82</td>
<td>0.0610</td>
<td>50.59</td>
<td>0.0793</td>
<td>61.52</td>
</tr>
<tr>
<td>-40°C</td>
<td>100 mA</td>
<td>0.0381</td>
<td>14.97</td>
<td>0.0608</td>
<td>45.73</td>
<td>0.0488</td>
<td>38.84</td>
<td>0.0691</td>
<td>53.63</td>
</tr>
<tr>
<td>-50°C</td>
<td>25 mA</td>
<td>0.0109</td>
<td>4.06</td>
<td>0.0433</td>
<td>32.56</td>
<td>0.0290</td>
<td>24.03</td>
<td>0.0594</td>
<td>46.08</td>
</tr>
<tr>
<td>-50°C</td>
<td>50 mA</td>
<td>0.0107</td>
<td>8.80</td>
<td>0.0299</td>
<td>22.47</td>
<td>0.0207</td>
<td>17.14</td>
<td>0.0410</td>
<td>31.84</td>
</tr>
<tr>
<td>-50°C</td>
<td>100 mA</td>
<td>0.0054</td>
<td>4.51</td>
<td>0.0152</td>
<td>11.46</td>
<td>0.0169</td>
<td>9.07</td>
<td>0.0190</td>
<td>14.75</td>
</tr>
</tbody>
</table>

**Summary**

Since the rationale of adding the electrolyte additives was to improve the high temperature resilience, it is significant that the discharge rate capability was significantly improved for many of the formulations investigated. For example, as displayed in FIG. 26, when the cells were discharged at -30°C discharge rate at -30°C. All of the cells containing the electrolyte additives were observed to outperform the baseline solution most dramatically. These results suggest that the lithium intercalation/de-intercalation kinetics are more favorable with the cells containing the electrolyte additives, presumably due to preferable SEI formation characteristics. In order to decipher the influence of the electrolyte additives upon the kinetics of the respective electrodes, detailed electrochemical characterization of the cells was performed, as described below.

After performing the rate characterization testing, a cycling test was performed on the cells at high temperature to determine their high temperature resilience. This included performing 20 cycles at 60°C, followed by electrochemical characterization. As illustrated in FIG. 28, the cells containing the LiBOB and FEC additives displayed the best initial capacity and capacity retention after being subjected to cycling at 60°C. One of the major objectives of performing the electrochemical characterization upon completing the cycling at high temperature was to determine the manner in which the various additives influenced the degradation rates at both the anodes and the cathodes.

Electrochemical Characteristics

It is believed that the improved rate capability at low temperatures of Li-ion cells that utilized these ester-based solutions is primarily due to improved mass transfer characteristics in the electrolyte (higher ionic conductivity) and facile kinetics of lithium intercalation/de-intercalation at the interface due to favorable film formation behavior at the electrode surfaces. To enhance this understanding, as well as the impact that the electrolyte additives have upon these factors, we have assessed the electrochemical characteristics of the systems using a number of techniques, including Tafel polarization measurements, Electrochemical Impedance Spectroscopy (EIS), and linear micro-polarization measurements.

To determine the lithiation/de-lithiation kinetics of the anodes and the cathodes of the various systems, Tafel polarization measurements of the MCMB-LiNiCoAlO2 cells were performed. The measurements were conducted on the cells while they were in a full state of charge (SOC) (OCV=4.07V) before and after each storage period. In all of these Tafel plots, there are distinct charge-transfer controlled regimes, where the overpotential increases linearly with log (i). The effect of mass transfer seems to be relatively insignificant which allows one to obtain kinetic parameters, such as the exchange current and the transfer coefficients. As illustrated in FIG. 29, improved lithium de-intercalation kinetics (i.e., higher limiting currents) were observed for the anodes in contact with the electrolytes possessing the FEC, and to a lesser extent the VC, electrolyte additives compared to the baseline formulation, suggesting that a desirable surface film has formed in these cases.

As illustrated in FIG. 30, in which the Tafel polarization measurements have been performed on the LiNiCoAlO2 cathodes at room temperature, all of the cells containing electrolyte additives appeared to display enhanced lithium kinetics (i.e., higher limiting current densities) compared to the baseline formulation. It was observed that the addition of LiBOB had the most beneficial effect upon the nature of the SEI layer on the cathode and the corresponding lithium kinetics.

Generally, the trends with regard to the observed lithium kinetics and how they depend upon electrolyte type tend to track well with temperature. For example, when Tafel measurements were performed on the MCMB anodes at low temperature, as displayed in FIG. 31, the cells containing the FEC were again observed to deliver improved performance over the baseline formulation. In addition, when the LiNiCoAlO2 cathodes were measured at -20°C, as shown in FIG. 32, a similar trend was observed compared to that displayed at 20°C, with the cell containing the LiBOB delivering the best performance.
performance. However, the level of performance enhancement was not quite as dramatic as observed at ambient temperatures, suggesting that the rate at which the kinetics change as a function of temperature is not uniform across the samples investigated.

Lithium-LiNi_{1/3}Ni_{2/3}Mn_{2/3}O_2 Systems

Methyl propionate-based electrolytes were further tested in lithium-LiNi_{1/3}Ni_{2/3}Mn_{2/3}O_2 systems. As shown in Figs. 33 and 34, an electrolyte containing 1.2 M LiPF_6 in EC+EMC+MP (20:20:60 v/v %)+4% FEC was approximately 75% efficient during its first room temperature cycle, and suffered only minimal losses after multiple discharge cycles.

Example 3

Methyl Propionate-Based and Ethyl Butyrate-Based Electrolyte Solutions Without Additives

In the current study, the electrolyte was selected to have a salt concentration of 1.2M and an ester content of 60% by volume. More specifically, the electrolytes 1.20M LiPF_6 in EC+EMC+MP (20:20:60 v/v %) and 1.20M LiPF_6 in EC+EMC+EB (20:20:60 v/v %) were demonstrated to operate effectively over a wide temperature range in MCMB-LiNiCoAlO_2 and Li_{1/3}Ti_{2/3}O_2-LiNiCoAlO_2 prototype cells. These electrolytes were compared with low temperature electrolyte generally performed very comparably with the baseline formulation, as illustrated in Table 12.

### TABLE 11

Results of capacity and impedance characterization at 20°C.

<table>
<thead>
<tr>
<th>Cell Number</th>
<th>Cell ID</th>
<th>Cell Weight (Grams)</th>
<th>Cell Weight (kg)</th>
<th>Initial Voltage</th>
<th>Initial Capacity (Ah)</th>
<th>Initial Watt-Hours</th>
<th>Discharge Energy (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K08B604-02</td>
<td>NEC-02</td>
<td>10.07</td>
<td>0.0101</td>
<td>3.852</td>
<td>0.303</td>
<td>1.102</td>
<td>105.42</td>
</tr>
<tr>
<td>K08B604-07</td>
<td>NEC-07</td>
<td>10.18</td>
<td>0.0102</td>
<td>3.763</td>
<td>0.312</td>
<td>1.139</td>
<td>112.20</td>
</tr>
<tr>
<td>K08B604-09</td>
<td>NEC-09</td>
<td>10.18</td>
<td>0.0102</td>
<td>3.763</td>
<td>0.307</td>
<td>1.122</td>
<td>110.24</td>
</tr>
<tr>
<td>K08B604-11</td>
<td>NEC-11</td>
<td>10.17</td>
<td>0.0102</td>
<td>3.763</td>
<td>0.310</td>
<td>1.133</td>
<td>111.42</td>
</tr>
<tr>
<td>K08B604-18</td>
<td>NA1-18</td>
<td>10.21</td>
<td>0.0102</td>
<td>3.767</td>
<td>0.310</td>
<td>1.129</td>
<td>116.64</td>
</tr>
<tr>
<td>K08B604-19</td>
<td>NA1-19</td>
<td>10.18</td>
<td>0.0102</td>
<td>3.768</td>
<td>0.304</td>
<td>1.108</td>
<td>108.78</td>
</tr>
<tr>
<td>K08B604-20</td>
<td>NA1-20</td>
<td>10.18</td>
<td>0.0102</td>
<td>3.767</td>
<td>0.305</td>
<td>1.111</td>
<td>109.10</td>
</tr>
<tr>
<td>K08B604-21</td>
<td>NA1-21</td>
<td>10.16</td>
<td>0.0102</td>
<td>3.767</td>
<td>0.302</td>
<td>1.103</td>
<td>108.58</td>
</tr>
<tr>
<td>K08B604-33</td>
<td>NA2-33</td>
<td>10.04</td>
<td>0.0100</td>
<td>3.767</td>
<td>0.300</td>
<td>1.093</td>
<td>108.96</td>
</tr>
<tr>
<td>K08B604-35</td>
<td>NA2-35</td>
<td>10.05</td>
<td>0.0100</td>
<td>3.763</td>
<td>0.309</td>
<td>1.128</td>
<td>112.21</td>
</tr>
<tr>
<td>K08B604-42</td>
<td>NA3-42</td>
<td>9.92</td>
<td>0.0099</td>
<td>3.762</td>
<td>0.315</td>
<td>1.141</td>
<td>115.09</td>
</tr>
<tr>
<td>K08B604-43</td>
<td>NA3-43</td>
<td>10.01</td>
<td>0.0100</td>
<td>3.760</td>
<td>0.310</td>
<td>1.128</td>
<td>112.72</td>
</tr>
<tr>
<td>K08B604-44</td>
<td>NA3-44</td>
<td>9.98</td>
<td>0.0100</td>
<td>3.762</td>
<td>0.305</td>
<td>1.113</td>
<td>111.54</td>
</tr>
<tr>
<td>K08B604-45</td>
<td>NA3-45</td>
<td>9.98</td>
<td>0.0100</td>
<td>3.755</td>
<td>0.294</td>
<td>1.071</td>
<td>107.31</td>
</tr>
<tr>
<td>K08C466-07</td>
<td>NMP-07</td>
<td>10.04</td>
<td>0.0100</td>
<td>3.751</td>
<td>0.293</td>
<td>1.071</td>
<td>106.73</td>
</tr>
<tr>
<td>K08C466-08</td>
<td>NMP-08</td>
<td>10.11</td>
<td>0.0101</td>
<td>3.754</td>
<td>0.307</td>
<td>1.120</td>
<td>110.76</td>
</tr>
<tr>
<td>K08C466-09</td>
<td>NMP-09</td>
<td>10.04</td>
<td>0.0100</td>
<td>3.752</td>
<td>0.297</td>
<td>1.086</td>
<td>108.11</td>
</tr>
<tr>
<td>K08C466-10</td>
<td>NMP-10</td>
<td>10.14</td>
<td>0.0101</td>
<td>3.746</td>
<td>0.307</td>
<td>1.123</td>
<td>110.67</td>
</tr>
</tbody>
</table>

K08C466-02 NEC-02 1.2 M LiPF_6 in EC+EMC (30:70 v/v %) (DoE, Baseline)
K08C466-03 NEC-03 1.2 M LiPF_6 in EC+EMC+EB (20:20:60 v/v %) (DoE, Baseline)
K08C466-04 NEC-04 1.2 M LiPF_6 in EC+EMC+MP (20:20:60 v/v %) (DoE, Baseline)
K08C466-05 NEC-05 1.2 M LiPF_6 in EC+EMC+MP (20:20:60 v/v %) (DoE, Baseline)
K08C466-06 NEC-06 1.2 M LiPF_6 in EC+EMC+MP (20:20:60 v/v %) (DoE, Baseline)
K08C466-07 NEC-07 1.2 M LiPF_6 in EC+EMC+MP (20:20:60 v/v %) (DoE, Baseline)
K08C466-08 NEC-08 1.2 M LiPF_6 in EC+EMC+MP (20:20:60 v/v %) (DoE, Baseline)
K08C466-09 NEC-09 1.2 M LiPF_6 in EC+EMC+MP (20:20:60 v/v %) (DoE, Baseline)
K08C466-10 NEC-10 1.2 M LiPF_6 in EC+EMC+MP (20:20:60 v/v %) (DoE, Baseline)

4) Quallion Low Temperature “A1”
5) Quallion Low Temperature “A2”
6) Quallion Low Temperature “A3”

A number of cells of each electrolyte type and cell chemistry (either MCMB-LiNiCoAlO_2 or Li_{1/3}Ti_{2/3}O_2-LiNiCoAlO_2) were manufactured and four cells of each permutation were used for performance assessment (36 cells total). These cells served to verify and demonstrate the reversibility, cycle life performance, low temperature performance, rate capability, and impedance characteristics.

A comprehensive test plan was established to determine the viability of the electrolytes to meet a number of performance metrics. The test plan consisted of implementing a number of performance tests, including the following: 1) initial characterization of all cells at 20, 0, and –20°C, 2) discharge characterization testing as a function of temperature and rate, and 3) variable temperature cycling over a wide temperature range.

Initial Characterization Testing

All cells were subjected to capacity and impedance characterization testing to determine the overall health of the cell. Regardless of electrolyte type, all cells generally displayed comparable capacity and excellent reproducibility from cell to cell. As shown in Fig. 35, all of the MCMB-LiNiCoAlO_2 cells were observed to deliver between 0.294 Ah to 0.312 Ah, and ranged between 99 to 111 Wh/kg, when evaluated at 20°C. In addition, Table 11 shows that all of the cells displayed comparable impedance, with the cells containing the 1.2M LiPF_6 in EC+EMC+MP (20:20:60 v/v %) electrolyte yielding the lowest average impedance (ave=95.8 mOhm) at 100% SOC, whereas the cells containing the Quallion “A3” low temperature electrolyte delivered the highest impedance (ave=115.1 mOhm).

When the cells were characterized at –20°C, all cells containing the advanced wide operating temperature range electrolyte generally performed very comparably with the baseline formulation, as illustrated in Table 12.
### TABLE 11-continued

Results of capacity and impedance characterization at 20° C.

<table>
<thead>
<tr>
<th>Cell Number</th>
<th>Cell ID</th>
<th>Cell Weight (Grams)</th>
<th>Cell Weight (kg)</th>
<th>Initial Voltage (Volts)</th>
<th>Initial Capacity (Ah)</th>
<th>Initial Watt-Hours (Wh/kg)</th>
<th>Calculated Impedance (mOhms) (100% SOC)</th>
<th>Calculated Impedance (mOhms) (80% SOC)</th>
<th>Calculated Impedance (mOhms) (60% SOC)</th>
<th>Calculated Impedance (mOhms) (40% SOC)</th>
<th>Electrolyte Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>K08C466-19</td>
<td>NEB-19</td>
<td>10.03</td>
<td>0.0100</td>
<td>3.758</td>
<td>0.286</td>
<td>1.047</td>
<td>104.33</td>
<td>105.59</td>
<td>108.03</td>
<td>104.98</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
<td>K08C466-20</td>
<td>NEB-20</td>
<td>10.54</td>
<td>0.0105</td>
<td>3.758</td>
<td>0.287</td>
<td>1.048</td>
<td>99.41</td>
<td>103.76</td>
<td>105.59</td>
<td>104.98</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
<td>K08C466-22</td>
<td>NEB-22</td>
<td>10.15</td>
<td>0.0101</td>
<td>3.756</td>
<td>0.304</td>
<td>1.110</td>
<td>109.38</td>
<td>101.93</td>
<td>106.20</td>
<td>106.20</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>10.11</td>
<td>0.0101</td>
<td>3.764</td>
<td>0.303</td>
<td>1.109</td>
<td>106.49</td>
<td>104.89</td>
<td>108.59</td>
<td>108.38</td>
<td>110.56</td>
</tr>
</tbody>
</table>

### TABLE 12

Results of capacity and impedance characterization at -20° C.

<table>
<thead>
<tr>
<th>Cell Number</th>
<th>Cell ID</th>
<th>Percent of RT Capacity (%)</th>
<th>Calculated Impedance (mOhms) (Charge at RT)</th>
<th>Calculated Impedance (mOhms) (100% SOC)</th>
<th>Calculated Impedance (mOhms) (80% SOC)</th>
<th>Calculated Impedance (mOhms) (60% SOC)</th>
<th>Calculated Impedance (mOhms) (40% SOC)</th>
<th>Electrolyte Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>K08B604-02</td>
<td>NEC-02</td>
<td>10.10</td>
<td>0.0101</td>
<td>0.2026</td>
<td>0.2503</td>
<td>0.2421</td>
<td>0.871</td>
<td>86.47</td>
</tr>
<tr>
<td>K08B604-07</td>
<td>NEC-07</td>
<td>10.10</td>
<td>0.0102</td>
<td>0.3121</td>
<td>0.2536</td>
<td>0.2382</td>
<td>0.855</td>
<td>84.19</td>
</tr>
<tr>
<td>K08B604-09</td>
<td>NEC-09</td>
<td>10.10</td>
<td>0.0102</td>
<td>0.3070</td>
<td>0.2501</td>
<td>0.2382</td>
<td>0.855</td>
<td>83.97</td>
</tr>
<tr>
<td>K08B604-11</td>
<td>NEC-11</td>
<td>10.10</td>
<td>0.0102</td>
<td>0.3302</td>
<td>0.2524</td>
<td>0.2411</td>
<td>0.866</td>
<td>85.12</td>
</tr>
<tr>
<td>K08B604-18</td>
<td>NAI-18</td>
<td>10.10</td>
<td>0.0102</td>
<td>0.3309</td>
<td>0.2585</td>
<td>0.2433</td>
<td>0.849</td>
<td>83.14</td>
</tr>
<tr>
<td>K08B604-19</td>
<td>NAI-19</td>
<td>10.10</td>
<td>0.0102</td>
<td>0.3046</td>
<td>0.2553</td>
<td>0.2312</td>
<td>0.805</td>
<td>79.06</td>
</tr>
<tr>
<td>K08B604-20</td>
<td>NAI-20</td>
<td>10.10</td>
<td>0.0102</td>
<td>0.3047</td>
<td>0.2587</td>
<td>0.2367</td>
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<td></td>
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<td>0.3032</td>
<td>0.2564</td>
<td>0.2336</td>
<td>0.815</td>
<td>81.62</td>
</tr>
</tbody>
</table>

Percent of RT Capacity: (Charge at -20° C.)

<table>
<thead>
<tr>
<th>Cell Number</th>
<th>Percent of RT Capacity at -20° C.</th>
<th>Calculated Impedance (mOhms) (Charge at -20° C.)</th>
<th>Electrolyte Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>K08B604-02</td>
<td>80.03</td>
<td>709.85</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
<td>K08B604-07</td>
<td>79.24</td>
<td>711.07</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
<td>K08B604-09</td>
<td>77.58</td>
<td>715.25</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
<td>K08B604-11</td>
<td>77.71</td>
<td>715.01</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
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<td>K08B604-19</td>
<td>76.68</td>
<td>667.73</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
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<td>76.80</td>
<td>656.75</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
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<td>694.59</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
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<td>361.33</td>
<td>JPL (EC + EMC + EB)</td>
</tr>
<tr>
<td>K08B604-42</td>
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<td>615.58</td>
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<tr>
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<td>672.59</td>
<td>JPL (EC + EMC + EB)</td>
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</tbody>
</table>
Discharge Characterization Testing (Room Temperature Charge)

A number of cells were subjected to comprehensive rate characterization over a wide range of temperatures (−60 to +20°C), using a range of discharge rates (C/20 to 5 C rates). In these tests, all of the cells were charged at ambient temperatures and discharged at the respective temperature of interest. As shown in Fig. 35, when the cells were evaluated at a modest discharge rate (C/10 rate, or 0.025 A) at −60°C, all of the cells containing the advanced low temperature electrolytes outperformed the baseline electrolyte system (expressed in terms of the discharge energy provided). As shown, the electrolyte containing 1.20M LiPF₆ in EC+EMC+MP (20:20:60 v/v%) provided the best performance followed by the cell containing one of the Quallion low temperature electrolytes (A3), both delivering over 50 Wh/kg at −60°C. In contrast, the baseline formulation delivered less than half of the energy under similar conditions.

As illustrated in FIG. 36, the cells were also able to support C/2 discharge rates at −60°C, when the cells are discharged to 2.0V. The same trends with regard to electrolyte type that were observed at the lower rates at this temperature were also observed with the higher rate discharge. However, the magnitude of the performance enhancement seen with the cells containing the low temperature electrolyte was more dramatic. For example, the cell containing 1.20M LiPF₆ in EC+EMC+MP (20:20:60 v/v%) provided nearly 50% of the room temperature capacity under these conditions, whereas the baseline all-carbonate based solution only delivered approximately one fifth of that amount, or ~10%.

The cells also displayed excellent performance when they were evaluated at more aggressive rates. As illustrated in FIG. 37, many of the cells were capable of supporting a 2 C discharge rate at −50°C, with the cell containing 1.20M LiPF₆ in EC+EMC+MP (20:20:60 v/v%) providing nearly 40 Wh/kg under these conditions, whereas the baseline formulation only delivered one fourth of that amount (i.e. 10 Wh/kg). It should be noted that in addition to providing high capacity and specific energy under conditions of high rate discharge at low temperatures, the cells containing the electrolytes of the present invention displayed less discharge polarization (i.e., less voltage drop). This observation is significant when considering applications which require high power capability at low temperatures, many of which have minimum operating voltage requirements. This behavior is illustrated in FIG. 38, in which the voltage profiles for a number of cells subjected to high rate discharge are displayed (i.e., 4.0 C rate, or 1.0 A discharge, at −40°C).

The high rate performance of a number of cells at −40°C containing the electrolytes of the present invention is summarized in Table 13. As illustrated, the methyl propionate-based electrolyte system, as well as Quallion’s “A1” and “A3” formulations, enable cells to perform well at high rates (up to 5 C), in contrast to the baseline DOE formulation. This is highlighted by FIGS. 39 and 40, in which the discharge capacity at various rates at −40°C is displayed for the baseline all-carbonate based solution and the methyl propionate-based solution, respectively.

### TABLE 13

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Rate (A)</th>
<th>Capacity (Ah)</th>
<th>Watt-Hours (Wh)</th>
<th>Energy (Wh/Kg)</th>
<th>% of Tₚ</th>
<th>Capacity (Ah)</th>
<th>Watt-Hours (Wh)</th>
<th>Energy (Wh/Kg)</th>
<th>% of Tₚ</th>
</tr>
</thead>
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<tr>
<td>NEC-09</td>
<td>1.2M LiPF₆ in EC + EMC (30:70)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20°C</td>
<td>C/5</td>
<td>0.050</td>
<td>0.3070</td>
<td>1.122</td>
<td>110.24</td>
<td>100</td>
<td>0.3102</td>
<td>1.133</td>
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<td>−40°C</td>
<td>5.0 C</td>
<td>1.250</td>
<td>0.0460</td>
<td>0.109</td>
<td>10.75</td>
<td>14.99</td>
<td>0.0528</td>
<td>0.127</td>
<td>12.46</td>
</tr>
<tr>
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<td>4.5 C</td>
<td>1.125</td>
<td>0.0544</td>
<td>0.132</td>
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<td>17.72</td>
<td>0.0929</td>
<td>0.154</td>
<td>15.16</td>
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<tr>
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<td>0.0607</td>
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<td>19.77</td>
<td>0.0691</td>
<td>0.172</td>
<td>16.88</td>
</tr>
<tr>
<td></td>
<td>3.5 C</td>
<td>0.875</td>
<td>0.0706</td>
<td>0.178</td>
<td>17.48</td>
<td>22.99</td>
<td>0.0820</td>
<td>0.209</td>
<td>20.55</td>
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<tr>
<td></td>
<td>3.0 C</td>
<td>0.750</td>
<td>0.0854</td>
<td>0.220</td>
<td>21.62</td>
<td>27.80</td>
<td>0.0972</td>
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<td>2.5 C</td>
<td>0.625</td>
<td>0.0941</td>
<td>0.247</td>
<td>24.29</td>
<td>30.60</td>
<td>0.1033</td>
<td>0.281</td>
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<td>2.0 C</td>
<td>0.500</td>
<td>0.1094</td>
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<td>28.92</td>
<td>35.63</td>
<td>0.1209</td>
<td>0.327</td>
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<tr>
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<td>1.5 C</td>
<td>0.375</td>
<td>0.1259</td>
<td>0.346</td>
<td>33.97</td>
<td>41.00</td>
<td>0.1351</td>
<td>0.373</td>
<td>37.63</td>
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<td>1.0 C</td>
<td>0.250</td>
<td>0.1515</td>
<td>0.429</td>
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<td>50.35</td>
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<tr>
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<td>0.1808</td>
<td>0.538</td>
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<td></td>
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<td>53.71</td>
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<tr>
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<td>0.050</td>
<td>0.2080</td>
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<td>0.2103</td>
<td>0.673</td>
<td>66.19</td>
</tr>
<tr>
<td>C/10</td>
<td>0.025</td>
<td>0.2257</td>
<td>0.752</td>
<td>73.88</td>
<td>75.32</td>
<td></td>
<td>0.2289</td>
<td>0.765</td>
<td>75.18</td>
</tr>
<tr>
<td>−50°C</td>
<td>5.0 C</td>
<td>1.250</td>
<td>0.1913</td>
<td>0.515</td>
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<td>62.78</td>
<td>0.1861</td>
<td>0.495</td>
<td>48.79</td>
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<tr>
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<td>0.1916</td>
<td>0.518</td>
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<td>62.88</td>
<td>0.1861</td>
<td>0.497</td>
<td>48.95</td>
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<tr>
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<td>0.1910</td>
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<td>62.67</td>
<td>0.1852</td>
<td>0.495</td>
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<td>3.5 C</td>
<td>0.875</td>
<td>0.1900</td>
<td>0.515</td>
<td>50.57</td>
<td>62.36</td>
<td>0.1851</td>
<td>0.497</td>
<td>48.91</td>
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<tr>
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<td>0.750</td>
<td>0.1908</td>
<td>0.520</td>
<td>51.09</td>
<td>62.62</td>
<td>0.1859</td>
<td>0.501</td>
<td>49.38</td>
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<td>0.1909</td>
<td>0.522</td>
<td>51.26</td>
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<td>0.1861</td>
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<td>49.65</td>
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<td>0.1953</td>
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<td>64.09</td>
<td>0.1918</td>
<td>0.530</td>
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<tr>
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<td>66.17</td>
<td>0.1985</td>
<td>0.562</td>
<td>55.38</td>
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<td>0.2144</td>
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<td></td>
<td>0.2117</td>
<td>0.624</td>
<td>61.45</td>
</tr>
</tbody>
</table>

Quallion Low Temperature
Electrolyte "A1"
phenomena, such as lithium plating on the anode which can lead to significant irreversible performance decline in the cells containing the Quallion-based electrolytes (A1, A2, and A3). This has been determined to be due to the fact that lithium plating was believed to have occurred on the anode when charging at low temperature, leading to irreversible capacity loss as evident by all subsequent cycling. In contrast, the present low temperature electrolyte systems do not display such phenomena and exhibit good capacity retention upon going to warmer temperatures. However, all of the electrolytes, the baseline all-carbonate based formulation yielded the best overall performance, including resilience to high temperature extremes and minimal lithium plating under these conditions (C/10 charging when cycled at lower temperatures, and C/5 discharging at all temperatures).

In addition to evaluating the variable temperature performance of MCMB-LiNiCoAlO$_2$ cells over a wide temperature range, we have also tested similar cells in which another type of anode material was used, namely lithium titanate, Li$_4$Ti$_5$O$_12$. This material is often referred to as a “zero strain” material and has been demonstrated to have good cycle life characteristics (K. M. Colbow, J. R. Dahn, and R. R. Haering, J. Power Sources, 26, 397 (1989)). The anode material possesses a flat operating voltage of ~1.5V vs. Li/Li$^+$, so present low temperature electrolyte systems do not display so present low temperature electrolyte systems do not display such phenomena and exhibit good capacity retention upon going to warmer temperatures.

As shown in FIG. 41, of the cells containing the advanced low temperature electrolytes of the present invention, those containing the methyl propionate and ethyl butyrate-based systems performed much better than the Quallion-based systems. As shown, the first 20 cycles performed at ~30°C led to significant irreversible performance decline in the cells containing the Quallion-based electrolytes (A1, A2, and A3). This has been determined to be due to the fact that lithium plating was believed to have occurred on the anode when charging at low temperature, leading to irreversible capacity loss as evident by all subsequent cycling. In contrast, the present low temperature electrolyte systems do not display such phenomena and exhibit good capacity retention upon going to warmer temperatures. However, all of the electrolytes, the baseline all-carbonate based formulation yielded the best overall performance, including resilience to high temperature extremes and minimal lithium plating under these conditions (C/10 charging when cycled at lower temperatures, and C/5 discharging at all temperatures).

In addition to evaluating the variable temperature performance of MCMB-LiNiCoAlO$_2$ cells over a wide temperature range, we have also tested similar cells in which another type of anode material was used, namely lithium titanate, Li$_4$Ti$_5$O$_12$. This material is often referred to as a “zero strain” material and has been demonstrated to have good cycle life characteristics (K. M. Colbow, J. R. Dahn, and R. R. Haering, J. Power Sources, 26, 397 (1989)). The anode material possesses a flat operating voltage of ~1.5V vs. Li/Li$^+$. The anode...
and is, thus, believed to not form a “solid electrolyte interface” due to electrolyte reduction. For these reasons, it has been identified to have potential to enable efficient operation at low temperatures, without the likelihood of lithium plating occurring, or other life limiting degradation processes which occur typically at carbon anodes (J. L. Allen, T. R. Jow, and J. Wolfenstein, J. Power Sources, 159, 1340-1345 (2006)). Thus, although the energy density of the cells can be significantly reduced, the introduction of such a material can be attractive for many applications, especially where long life is need under extreme conditions.

As shown in FIG. 42, when lithium titanate-based cells containing a number of electrolytes under evaluation were subjected to similar variable temperature cycling over a wide temperature range, much more stable performance was observed in all cases. Of note is the fact that the cells containing the Quallion based electrolyte “A1” did not display irreversible capacity loss upon being cycled at lower temperatures, in contrast to the MCMB carbon anode based systems. It should also be noted that the charge and discharge rates for these tests were C/2 for all temperatures, representing an aggressive charge condition where dramatic lithium plating would certainly occur with the carbon based analogues. Thus, it appears as though lithium titanate is an anode material of choice for applications which require long life, and when coupled with the appropriate advanced electrolytes can provide good cycle life and power capabilities over a wide temperature range. In addition to performing cycling tests, we have also obtained excellent discharge characteristics with this system with the methyl propionate-based system and the Quallion “A1” electrolytes.

SUMMARY AND CONCLUSIONS

We have demonstrated two electrolytes, namely 1.20M LiPF$_6$ in EC+EMC+MP (20:20:60 v/v %) and 1.20M LiPF$_6$ in EC+EMC+EB (20:20:60 v/v %), to operate effectively over a wide temperature range in MCMB-LiNiCoAlO$_2$ and Li$_4$Ti$_5$O$_12$-LiNiCoAlO$_2$ prototype cells. These electrolytes have enabled high rate performance at low temperature (i.e., up to 2.0 C rates at $-50^\circ$ C and 5.0 C rates at $-40^\circ$ C) and good cycling performance over a wide temperature range (i.e., from $-40^\circ$ C to $+70^\circ$ C.).

STATEMENTS REGARDING INCORPORATION BY REFERENCE AND VARIATIONS

All references throughout this application, for example patent documents including issued or granted patents or equivalents; patent application publications; and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entirety, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the invention has been specifically disclosed by preferred embodiments, exemplary embodiments and optional features, modification and variation of the concepts herein disclosed can be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims. The specific embodiments provided herein are examples of useful embodiments of the invention and it will be apparent to one skilled in the art that the invention can be carried out using a large number of variations of the devices, device components, and method steps set forth in the present description. As will be apparent to one of skill in the art, methods and devices useful for the present methods can include a large number of optional composition and processing elements and steps.

When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups, including any isomers, enantiomers, and diastereomers of the group members, are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure. When a compound is described herein such that a particular isomer, enantiomer or diastereomer of the compound is not specified, for example, in a formula or in a chemical name, that description is intended to include each isomer and enantiomer of the compound described individually or in any combination. Additionally, unless otherwise specified, all isotopic variants of compounds disclosed herein are intended to be encompassed by the disclosure. For example, it will be understood that any one or more hydrogens in a molecule disclosed can be replaced with deuterium or tritium. Isotopic variants of a molecule are generally useful as standards in assays for the molecule and in chemical and biological research related to the molecule or its use. Methods for making such isotopic variants are known in the art. Specific names of compounds are intended to be exemplary, as it is known that one of ordinary skill in the art can name the same compounds differently.

It must be noted that as used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to “a cell” includes a plurality of such cells and equivalents thereof known to those skilled in the art, and so forth. As well, the terms “or” (or “an”), “one or more” and “at least one” can be used interchangeably herein. It is also to be noted that the terms “comprising”, “including”, and “having” can be used interchangeably. The expression “of any of claims XX-YY” (wherein XX and YY refer to claim numbers) is intended to provide a multiple dependent claim in the alternative form, and in some embodiments is interchangeable with the expression “as in any one of claims XX-YY.”

Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be utilized in the practice or testing of the present invention, the preferred methods and materials are now described. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

Every formulation or combination of components described or exemplified herein can be used to practice the invention, unless otherwise stated. Whenever a range is given in the specification, for example, a range of integers, a temperature range, a time range, a composition range, or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. As used herein, ranges specifically include the
values provided as endpoint values of the range. As used herein, ranges specifically include all the integer values of the range. For example, a range of 1 to 100 specifically includes the end point values of 1 and 100. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art as of their publication or filing date and it is intended that this information can be employed herein, if needed, to exclude specific embodiments that are in the prior art. For example, when compositions of matter are claimed, it should be understood that compounds known and available in the art prior to Applicant's invention, including compounds for which an enabling disclosure is provided in the references cited herein, are not intended to be included in the composition of matter claims herein.

As used herein, “comprising” is synonymous and can be used interchangeably with “including,” “containing,” or “characterized by,” and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, “consisting of” excludes any element, step, or ingredient not specified in the claim element. As used herein, “consisting essentially of” does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms “comprising”, “consisting essentially of” and “consisting of” can be replaced with either of the other two terms. The invention illustratively described herein suitably can be practiced in the absence of any element or elements, limitation or limitations which is/are not specifically disclosed herein.

One of ordinary skill in the art will appreciate that starting materials, biological materials, reagents, synthetic methods, purification methods, analytical methods, assay methods, and biological methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed can be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

We claim:
1. An electrolyte for use in an electrochemical cell, the electrolyte comprising a mixture of:
   - 15-30% by volume cyclic carbonate, wherein the cyclic carbonate is a combination of mono-fluoroethylene carbonate (FEC) and EC wherein the FEC is present in an amount from 0.5 to 10% by volume;
   - 15-30% by volume non-cyclic carbonate, wherein the non-cyclic carbonate is selected from ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl propyl carbonate (MPC) and combinations thereof;
   - 40-70% by volume non-fluorinated linear ester, wherein the non-fluorinated linear ester is selected from: methyl propionate, ethyl propionate, methyl butyrate, ethyl butyrate, propyl butyrate, butyl butyrate, and combinations thereof; and
   - a lithium salt in a concentration from 0.5 M to 1.5 M.
2. The electrolyte of claim 1, wherein the non-cyclic carbonate is ethyl methyl carbonate (EMC), the lithium salt includes LiPF₆ in a concentration from 0.8 to 1.20 M and the non-fluorinated linear ester is selected from methyl propionate, methyl butyrate and combinations thereof.
3. The electrolyte of claim 1, wherein at least two non-fluorinated linear esters are present, a first non-fluorinated linear ester having a low viscosity and selected from the group consisting of methyl propionate, ethyl propionate, methyl butyrate and ethyl butyrate and a second non-fluorinated linear ester having a high viscosity and selected from the group consisting of propyl butyrate and butyl butyrate.
4. The electrolyte of claim 1 further comprising an additive selected from lithium oxalate, lithium bis(oxalato)borate (LiBOB), vinylene carbonate (VC), lithium difluoro-oxalate borate (LiDFOB) and combinations thereof.
5. The electrolyte of claim 1 further comprising an additive selected from lithium bis(oxalato)borate (LiBOB), lithium difluoro-oxalate borate (LiDFOB) and combinations thereof in a concentration of 0.05 to 0.25 M.
6. The electrolyte of claim 1 wherein the FEC is present in an amount from 2 to 10% by volume.
7. The electrolyte of claim 1 wherein the FEC is present in an amount from 0.5 to 5% by volume.
8. An electrochemical cell comprising:
   - an anode;
   - the electrolyte of claim 1 provided between the anode and the cathode.
9. The electrochemical cell of claim 8, wherein the cathode comprises a material selected from LiCoO₂, LiMn₂O₄, LiNi₀.₅Co₀.₅Mn₁.₅O₄, LiNiₓCo₀ₓMn₁-xO₂, LiNi₁₋ₓCoxMnₓO₂, Li(LiₓNi₄₋ₓMn₄ₓ)O₂ layered-layered composite LiNi-Co-Mn-O, or LiNiₓMn₄₋ₓO₄.
10. The electrolyte of claim 8, wherein the anode comprises a material selected from natural graphite, synthetic graphite, hard carbon, mesocarbon microbeads (MCM), silicon-carbon composites, lithium titanate (Li₄Ti₅O₁₂), lithium metal and combinations thereof.
11. The electrochemical cell of claim 8 wherein the anode is a carbon-based anode and the cathode is selected from LiFePO₄, LiNiCoO₂, LiNiCoAlO₂, and a layered-layered composite of LiNiCoMnO₂, LiNiₓMn₄₋ₓO₄ or Li NiₓMn₄₋ₓCoxMnₓO₂.
12. A method of making an electrochemical cell comprising the steps of: providing a cathode; providing an anode; and providing the electrolyte of claim 1 between the cathode and the anode.
13. A method of generating an electrical current, the method comprising the steps of: providing an electrochemical cell according to claim 8, the cell being in a charged state; and discharging the electrochemical cell.

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