The Effect of Electrolyte Additives Upon the Kinetics of Lithium Intercalation/De-Intercalation at Low Temperatures

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Objective

- Develop low temperature electrolytes which will enable the operation of lithium-ion cells over a wide range of temperatures (-40° to +40°C) for future Mars missions (enabling Landers and Rovers).

Approach

- Develop improved electrolyte formulations that possess high conductivity over a range of temperatures, good electrode passivation characteristics, and good electrochemical and chemical stability to enable the operation of lithium ion cell at temperatures as low as -50°C.

- Evaluate candidate electrolytes in experimental Li-carbon, Li-LiNiCoO$_2$, and MCMB-LiNoCoO$_2$ three-electrode cells (with pseudo Li reference).

- Investigate the viability of using electrolyte additives to improve the kinetics of lithium intercalation/de-intercalation (especially at low temperature).
Background

- Researchers from SAFT have demonstrated improved performance of lithium-ion cells containing electrolytes with VC (decreased irreversible capacity losses, improved life characteristics, improved tolerance to high temperature exposure).

- Using density functional theory calculations, researchers have studied the fundamental reductive decomposition reactions involved with the use of vinylene carbonate in lithium-ion battery environments.

- Using spectroscopic techniques, researchers have suggested that VC polymerizes on the lithiated graphite surfaces, forming poly alkyl Li-carbonate species that suppress both solvent and salt anion reduction. Aurbach and coworkers have also demonstrated that VC also interacts with cathode materials, and can result in better cathode kinetics (reduced impedances).
Background

- Vinylene carbonate (VC) is an unsaturated analogue to ethylene carbonate.

- A similar concept of using unsaturated analogues of oxygenated lithium-based electrolyte solvents was invested in the context of Li-TiS$_2$ systems (i.e., the use of 2-methylfuran in THF/2-MeTHF-based solutions).

  ➢ Abraham and coworkers (EIC)

2-Methylfuran  Tetrahydrofuran (THF)  2-Methyltetrahydrofuran (THF)
Experimental MCMB-LiNi$_{0.8}$Co$_{0.2}$O$_2$ Carbon Cells

Electrolytes Selected for Evaluation in Experimental Cells

- 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:2 v/v)
- 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v)
- 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:4 v/v)
- 1.0 M LiPF$_6$.EC+ DMC+EMC (15:15:70 v/v)
- 0.6 M LiPF$_6$ EC+DEC+DMC+EMC (1:3:3:3 v/v)
- 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:4 v/v)
- 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:4 v/v)
  + 1.5% Vinlylene Carbonate (VC)

- MCMB Carbon-LiNiCoO$_2$ Cells
- 400-450 mAh Size Cells
- All Cells equipped psuedo Li metal reference electrodes
- Flooded electrolyte design (cylindrical cells)

Techniques Used to Study the Low Temperature Characteristics

- Charge/discharge behavior at various temperatures
- Electrochemical Impedance Spectroscopy (EIS)
- DC Polarization Techniques
Effect of Electrolyte Additives on Cell Performance:
Low Temperature Performance in Experimental MCMB-LiNi$_{x}$Co$_{1-x}$O$_2$ Cells
Formation Characteristics

**MCMB Carbon-LiNi$_{x}$Co$_{1-x}$O$_2$ Cell**
25 mA Charge current to 4.1 V
25 mA Discharge current to 3.0 V
Temp = 23°C

- 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:4)
- 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:4) + VC

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Formation Characteristics of MCMB-LiNiCoO₂ Experimental Cells

Evaluation of Quaternary Carbonate Low Temperature Electrolytes

**MCMB Carbon-LiNiCoO₂ Cell**

1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4)

25 mA Charge current to 4.1 V
25 mA Discharge current to 3.0 V

Temp = 23°C

- 1st Discharge
- 2nd Discharge
- 3rd Discharge
- 4th Discharge
- 5th Discharge

**Discharge Capacity (Ahr)**

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A number of low EC-content electrolytes have been shown to have good low temperature performance characteristics.

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Effect of Electrolyte Additives on Cell Performance:
Low Temperature Performance in Experimental MCMB-LiNi$_x$Co$_{1-x}$O$_2$ Cells

- 1.00 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:4)
- 1.00 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:3)
- 1.00 M LiPF$_6$ EC+DMC+DEC +EMC (1:1:1:2)

Of the quaternary-based electrolytes, 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:3) was observed to display the best performance down to -50°C.
Effect of Electrolyte Additives on Cell Performance:
Low Temperature Performance in Experimental MCMB-LiNi\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{2} Cells
Discharge Capacity at Low Temperature (RT Charge)

Temp = - 20°C (~C/8 Rate)

![Graph showing discharge capacity at -20°C]

Temp = - 40°C (~C/16 Rate)

![Graph showing discharge capacity at -40°C]

➤ When vinylene carbonate (VC) was added to a MCMB-LiNi\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{2} cell containing a quaternary-based electrolyte, improved low temperature discharge capacity was observed at -20 and -40°C.
The addition of \textit{vinylene carbonate (VC)} was observed to result in lower film resistance, suggesting improved Li-ion migration through the electrode surface films.
Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells

EIS Measurements at 23°C

Use of Vinylene Carbonate (VC)

Cathode Measurements

Anode Measurements

- When the impedance spectra were compared for each electrode, the cathode was observed to display lower film resistance values, whereas, the anode displays higher resistance.
Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells

EIS Measurements at −20°C (Full Cell)

Use of Vinylene Carbonate (VC)

**MCMB Carbon-LiNi$_{x}$Co$_{1-x}$O$_2$ Cell**
(with lithium reference electrode)
Cell in Full SOC (OCV = −4.085V)

**Full Cell Measurements**

- 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:4) + 1.5%L vinylene carbonate
- 1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:4)

**Temperature = −20°C**
Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells
EIS Measurements at – 20°C
Use of Vinylene Carbonate (VC)

Cathode Measurements

Anode Measurements

Temperature = - 20°C

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Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells

EIS Measurements at -40°C (Full Cell)

*Use of Vinylene Carbonate (VC)*

**MCMB-LiNiCoO₂ Cells**

Cells in Full SOC (OCV=-4.085V)

*Temperature = -40°C*

- **1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4)**
- **1.0 M LiPF₆ EC+DMC+DEC +EMC (1:1:1:2)**
- **1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4) + 1.5% vinylene carbonate**
Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells
EIS Measurements at \(-40^\circ\text{C}\)

Use of Vinylene Carbonate (VC)

Cathode Measurements

Anode Measurements

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Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (-20°C)

Temperature = -20°C

1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4)

50 mA Charge Current to 4.1 V
0.001 A Taper Current Cut-Off

Cell Voltage (V vs Li/Li⁺)

Cathode

Anode

Cell Voltage

Current

Anode Potential (V vs Li/Li⁺) and Charge Current (A)

Time (Hours)
Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (-20°C)

Temperature = -20°C

1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4) + VC

50 mA Charge Current to 4.1 V
0.001 A Taper Current Cut-Off

Cell Voltage (V vs Li/Li⁺) and Anode Potential (V vs Li/Li⁺) and Charge Current (A)

Cell Voltage
Cathode
Anode
Current

-0.067 V

Time (Hours)

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Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (-20°C)

Temperature = -20°C

50 mA Charge Current to 4.1 V
0.001A Current Cut-Off

-67 mV vs. Li+/L

Cathode = 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4)
Cathode = 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4) +VC
Anode = 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4)
Anode = 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4) +VC
Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Effect of Charging at Low Temperature (-20°C)

- 50 mA Discharge Current
- Temperature = -20°C

No Evidence of Li Plating

1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4) + VC

- Room Temperature Charge
- Charged at Low Temperature (50mA to 4.1V)
Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (-30°C)

Cell Voltage

- 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4) +VC
- 70 mA Charge Current to 4.1 V
- 0.001 A Taper Current Cut-Off

Temperature = -30°C

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Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells:
Effect of Charging at Low Temperature (-30°C)

25 mA Discharge Current
Temperature = -30°C

Evidence of Lithium Plating

1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4) +VC

- Room Temperature Charge
- Charged at -30°C (70 mA to 4.1 V)
Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (-40°C)

MCMB-LiNiCoO2 Cell
1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4) +VC

Temperature = -40°C

25 mA charge current to 4.1 V
0.001 A Taper current cut-off

Cell Voltage (V vs Li/Li⁺) and Cathode Potential (V vs Li/Li⁺)

Anode Potential (V vs Li/Li⁺) and Charge Current (A)

Time (Hours)
Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Effect of Charging at Low Temperature (-40°C)

25 mA Discharge Current

Temperature = -40°C

Strong Evidence of Lithium Plating

1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4) + VC

- Room Temperature Charge
- Charged at Low Temperature (25 mA to 4.1V)

Discharge Capacity (Ahr)
Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (-40°C)

Temperature = -40°C

1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:4)

25mA Charge Current to 4.1 V
0.001 A Taper Current Cut-Off

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Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Effect of Charging at Low Temperature (-40°C)

Temperature = -40°C

25 mA Discharge Current

1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4)

- Room Temperature Charge
- Charged at -40°C (25 mA to 4.1 V)
Linear Polarization Measurements

* At low overpotentials (<RT/\alpha nF) the electrochemical rate equation can be linearized resulting in a linear current-potential relation.

* The curves were obtained under potentiodynamic conditions at scan rates of 0.02 mV/sec.

* The polarization resistance, or the exchange current density, can be calculated from the slopes of the linear plots.

* The electrodes were tested in near full state of charge and biased over a 10 mV range.

* The resulting polarization resistance value is indicative of the facility of both the lithium intercalation and de-intercalation processes in the material (encompassing Li+ diffusion through the SEI layer as well as bulk diffusion in the carbon electrode).

> Polarization resistance is observed to be higher for the cathode with most systems.
> Good tool to investigate kinetics at different temperatures as a function of electrolyte type.
Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Linear Micropolarization Measurements at Low Temperature

Temperature = -20°C

1. Cathode - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4) +VC
2. Cathode - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4)
3. Anode - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4) +VC
4. Anode - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4)
Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Linear Polarization Measurements at Low Temperature

Temperature = -40°C

1. Cathode - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4) +VC
2. Cathode - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4)
3. Anode - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4) +VC
4. Anode - 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:4)
At low temperatures, the VC-containing electrolyte results in improved kinetics at the cathode (lower polarization resistance) and poorer lithium kinetics at the anode.
Tafel Polarization Measurements of MCMB and LiNiCoO₂ Electrodes
Effect of Electrolyte upon Polarization at Different Temperatures

- Tafel polarization measurements allow further insight into the kinetics of lithium intercalation/de-intercalation on MCMB anodes and LiNiCoO₂ cathodes in these electrolytes.

- These measurements were made at scan rates slow enough (0.5 mV/s) to provide near-steady state conditions and yet with minimal changes in the state of charge of the electrode or its surface conditions.

- The cells were tested in near full state of charge and biased over a 150 mV range.

- Both anode and cathode polarization characteristics were measured at various different temperatures (23, 0, -20 and -40°C).

> In most cases, the cathode displays poorer kinetics and is performance limiting.
At low temperatures, the VC-containing electrolyte results in higher cathode electrode limiting current densities and lower anode electrode limiting current densities.
Conclusions

- Vinylene carbonate observed to improve low temperature performance
  * Higher discharge capacities observed at –20 and –40°C (RT charge)

- Lithium plating was observed to occur with low temperature charging
  * Use of vinylene carbonate in carbonate-based electrolytes shown to result in negative anode potentials under certain condition (high rate charge at low T)
  * Evidence of Li plating observed with very negative potentials (< -50 mV)
    (Especially when potential is not positive at any time during charge)
  * Increased anode polarization observed to be conducive to plating
  * Conditions for lithium plating at low temperature are also facilitated if low cathode polarization is observed
  * In most cases, plating is not observed due greater cathode polarization effects compared to the corresponding anode polarization
  * A low taper current cut-off on charge is preferred to avoid plating effects

- Determined that the electrolyte additives can have a profound impact of upon high rate charge and discharge at low temperature and the possibility of lithium plating.
Conclusions (Continued)

Results of Electrochemical Characterization

* EIS results indicate that the film and charge transfer resistances are lower for the cell incorporating the VC-containing electrolyte (full cell measurements).
* Individual electrode measurements indicate that this improvement is primarily attributable to improvements in the cathode electrode properties.
* Linear micropolarization and Tafel polarization measurements correlate well with the EIS measurements performed and indicate that the cathode kinetics (rather than the anode kinetics) are improved with the addition of VC).

General Observations and Conclusions

* Although VC may impart many favorable characteristics (protective SEI properties, minimal irreversible loss, good tolerance to high temperature extreme), for improved low temperature performance (including charge at low temperature) the use of VC as an electrolyte additive may not be preferred for all systems.
  * This conclusion must be made in the context of all carbonate-based electrolyte which generally result in favorable anode filming properties.
  * **VC appears to have more benefit when coupled with “aggressive” solvents (such as low viscosity ester co-solvents) which otherwise would result in electrode films (especially on the anode) that prove to be highly resistive.**
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