Fluorinated Ester Co-solvents for Low-Temperature Li-Ion Cells

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Outline

- Introduction
- Objective and Approach
- Background
- Experimental
- Approach and Methodology
- Assessment of Fluorinated Esters
  - MCMB-$LiNiCoO_2$ experimental full-cell results
    - Charge/discharge characteristics of MCMB cells
    - Electrochemical characterization:
      - EIS
      - D.C. micropolarization
      - Tafel polarization
- Conclusions

Functions of Rechargeable Batteries in Space Missions

- Rechargeable batteries are utilized to provide power
  - during launch and post-launch (until the deployment of solar panels in Inner planetary missions)
  - For firing pyros and firing rockets for attitude control,
  - To correct cruise anomalies or support trajectory control maneuvers of the spacecraft,
  - To the spacecraft, its equipment and payload during Sun eclipse periods,
  - For nighttime or eclipse-time experimentation,
  - For communicating and data transmission,
  - To keep the electronics warm and for
  - Load leveling (to augment nuclear power source)

Desired Characteristics of Space Batteries

- Light weight and compact for reducing the launch costs and maximizing payload and science instruments
- Ability to operate under extreme (low) temperatures for atmospheric and surface missions
  - Surface temperatures as low as -120°C e.g., Mars and Titan (Saturn's Moon)
  - Low temperature performance critical for missions to Moon, Mars and Beyond (especially with solar powered missions)
  - Low temperature performance is essential even in missions with nuclear power sources.
  - Preferred option to expending energy towards warming the battery
- Good cycle life, e.g. orbiter missions and satellites
- Long calendar life
- Safety, especially in human exploration missions
  - Astronaut's suit
  - Crew Exploration Vehicle
  - Planetary stations (Habitat)

Low Temperature Lithium Ion Electrolytes
Electrolyte Development: Approach/Background

- High conductivity over a wide range of temperatures
  - 1 mS cm-1 from –60 to 40°C
- Wide liquid range (low melting point)
  - -60 to 75°C
- Good electrochemical stability
  - Stability over wide voltage window (0 to 4.5V)
  - Minimal oxidative degradation of solvents/salts
- Good chemical stability
- Good compatibility with chosen electrode couple
  - Good SEI characteristics on electrode
  - Facile lithium intercalation/de-intercalation kinetics
- Good thermal stability
- Good low temperature performance throughout life of cell
  - Good resilience to high temperature exposure
  - Minimal impedance build-up with cycling and/or storage

Fluorinated Materials in Lithium-Ion Batteries

- Fluorinated Ethers
  - Methyl nonfluorobutyl ether [1]
    - Nonflammable characteristics as a cosolvent
- Fluorinated Amides
  - N,N-dimethyl trifluoroacetamide (DTA) [2] cosolvent/additive provides
    - Beneficial filming behavior
    - Satisfactory oxidation stability
    - Low melting point, high boiling point suggest improved low temperature performance and higher safety
- Fluorocarbonates
  - Most commonly used fluorinated additives/cosolvents
    - Fluoroethylne carbonate [3] and trifluoropropylne carbonate [4,5] extensively studied

1) Arai, J., *J. Electrochem. Soc.*, **2003**, *150*, A219-A228.

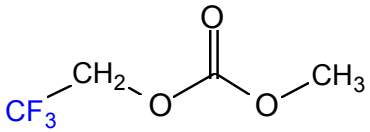
2) Winter, et. Al., *J. Power Sources*, **2001**, *97-98*, 595-597.

3) Shu, Z.X.; McMillan, R.S.; Murray, J.J.; Davidson, I.J., *J.Electrochem.Soc.*, **1996**, *143*, 2230.

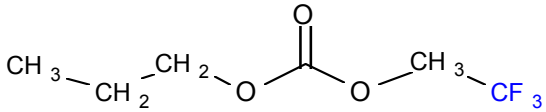
4) R. McMillan, H. Slegr, Z. X. Shu, and W. Wang, *J Power Sources*, **81-82**, 20 (1999).

5) M. Nagayama, *et al*, Ext. Abs. 1995 Fall Meeting of the Electrochem. Soc. of Japan, Kofu, Japan, p. 162 (1995).

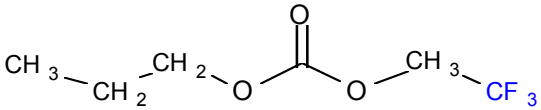
Fluorinated Carbonate Work Performed at JPL



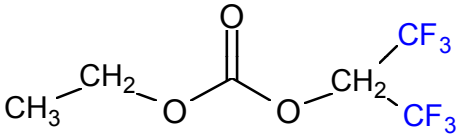
Methyl 2,2,2-trifluoroethyl carbonate
(MTFEC)



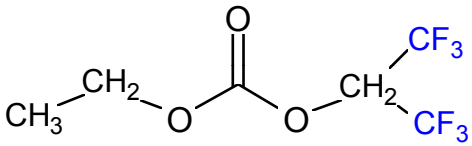
Propyl trifluoroethyl carbonate
(PTFEC)



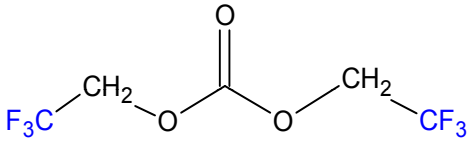
Propyl trifluoroethyl carbonate
(PTFEC)



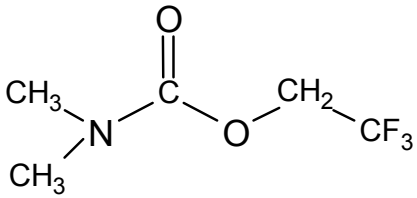
Ethyl hexafluoro- *i*-propyl carbonate
(EHFPC)



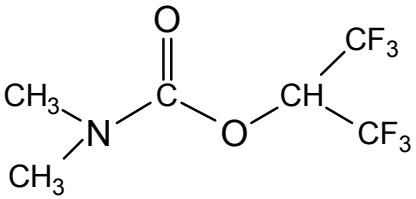
Ethyl hexafluoro-*i*-propyl carbonate
(EHFPC)



di-2,2,2-trifluoroethyl carbonate (DTFEC)



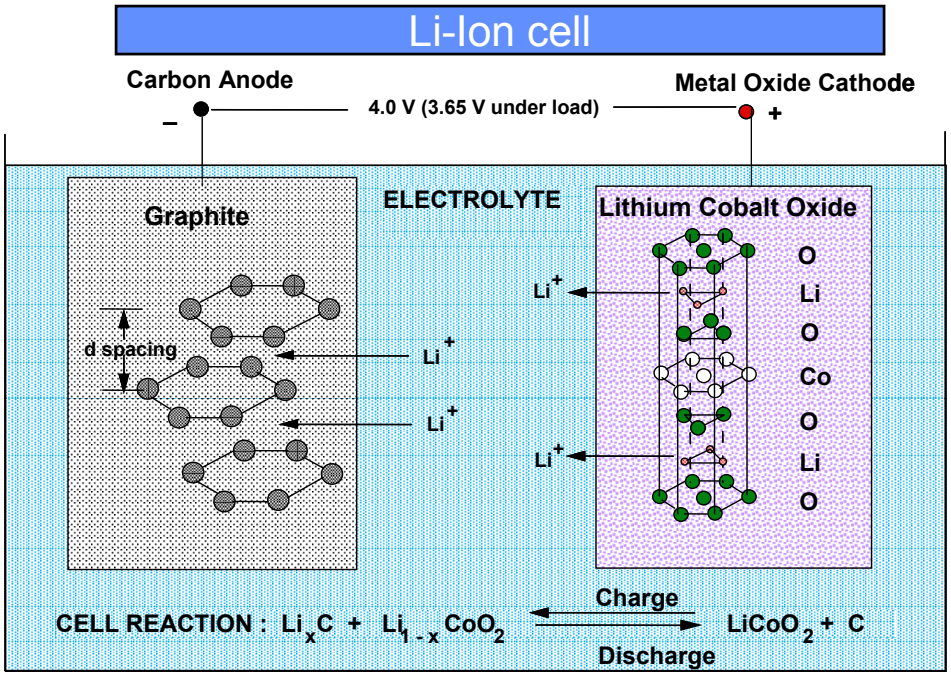
N,N-dimethyl 2,2,2-trifluoroethyl carbamate
(DMTFEC m)



N,N-dimethyl hexafluoro-iso-propyl carbamate
(DMHFPCm)

M. C. Smart, B. V. Ratnakumar, and S. Surampudi G. K. S. Prakash, J. Hu, and I. Cheung, "Improved Performance and Safety of Lithium Ion Cells with the Use of Fluorinated Carbonate Based Electrolytes", *J. Power Sources,* **119-12**, 359-367 (2003).

Surface Films on Electrodes in Li-ion Cells



Components

- Anode Materials
  - Intercalation anode
  - MCMB Carbons
  - Graphite or Coke
  - Lithium titanate
- Cathode Materials
  - Oxides $LiCoO_2$, $LiNi_xCo_{1-x}O_2$, $(LiNiMn)O_2$, $LiMn_2O_4$
  - $LiFePO_4$
- Electrolyte Materials
  - Salt: Typically 1.2 M $LiPF_6$
  - Solvents: Linear and cyclic carbonate mixtures
  - Co-solvents: Low viscosity co-solvents

- The success of Li-ion batteries may be entirely attributed to the surface film on the (carbon) anode – termed as the "Solid Electrolyte Interphase", which provides kinetic stability to an otherwise (thermodynamically) unstable system.
- Similar surface films reportedly exist on the cathodes as well

The Use of Fluoroesters as Li-ion Battery Electrolyte Co-Solvents

- Fluoroesters may improve lithium-ion cell performance in a multitude of ways
  - Low viscosity and lower melting points of carbonate based mixtures
  - Improved film forming properties
  - Partial flame retardancy

- Conceptual work performed by T. Nakajima, et. al. have provided proof of this concept
  - Initial studies of the electrochemical behavior of graphite electrode in electrolytes consisting of 1.0M $LiCl_4$ with EC+DEC+fluoroester at low temperatures [1,2]

- Previous studies on fluoroester have demonstrated numerous advantages
  - Improved low temperature performance [2]
  - Higher reductive potential yields intriguing film forming properties [2]
  - Increased capacity and coulombic efficiencies [3]

1) T. Nakajima, et. al., J. Fluorine Chem. **87**, 221 (1998).
2) T. Nakajima, et. al., J. Fluorine Chem. , **111**, 167-174 (2001).
3) T. Nakajima, et. al., J. New Materials for Electrochemical Systems, **8,** 181-189 (2006)

Fluoroesters as Lithium-Ion Batteries Co-Solvents

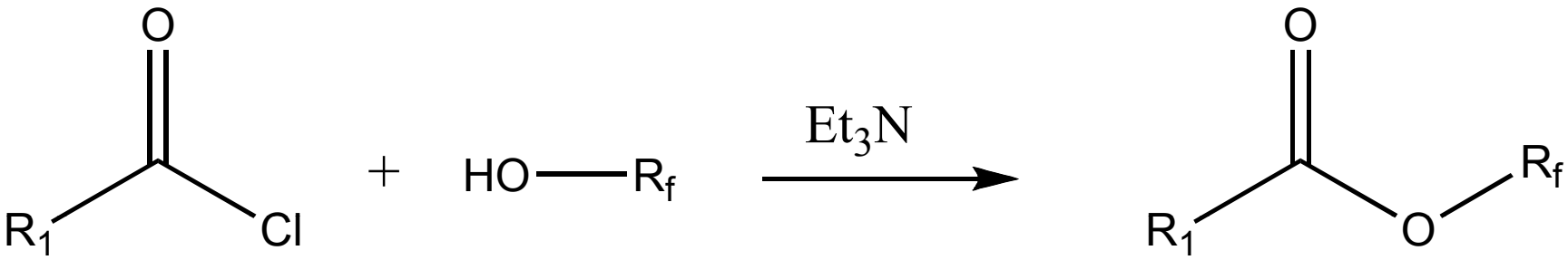
Objective:

Assess the viability of using fluorinated ester co-solvents in lithium-based electrolytes to improve the operating temperature range (-60 to + 60°C) and safety of Li-ion cells and batteries.

Approach:

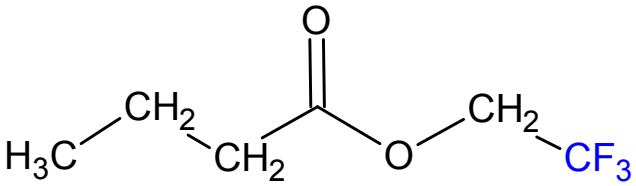
- Assess various fluorinated co-solvents, including fluorinated carbonates, carbamates, and esters, in multi-component electrolyte formulations
- Perform electrochemical characterization of advanced electrolytes (i.e., cyclic voltammetry and conductivity measurements).
- Assess performance of candidate electrolytes in experimental cells (i.e., Li-MCMB carbon cells and MCMB-$LiNi_xCo_{1-x}O_2$ cells)
  - Perform electrical characterization (charge/discharge behavior) over a wide temperature range (-60 to +65°C)
  - Perform electrochemical characterization (EIS, linear polarization, Tafel polarization measurements) over a wide temperature range (-60 to +25°C)

Synthesis of Fluorinated Esters



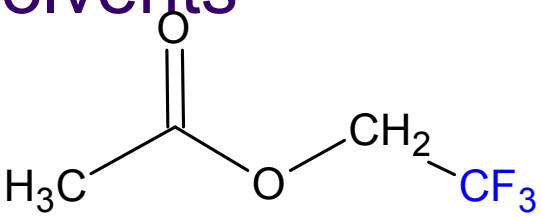
- Esterification Reaction
  - Simple
  - High Yield
- Purified via distillation under inert gas
- NMR clean

The Use of Fluoroesters as Potential Li-ion Battery Electrolyte Co-Solvents



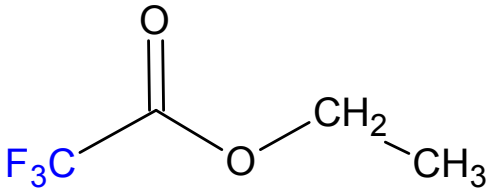
2,2,2-trifluoroethyl butyrate

(TFEB)



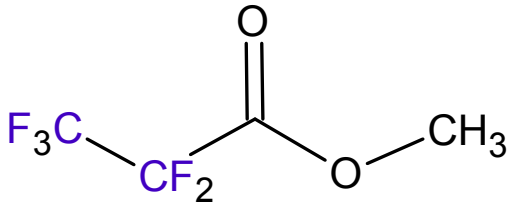
2,2,2-trifluoroethyl acetate

(TFEA)



ethyl trifluoroacetate

(ETFA)



methyl pentafluoropropionate

(MPFP)

In addition to imparting desirable physical properties to the electrolyte solutions, the solvents are envision to produce desirable SEI filming characteristics at carbon anodes.

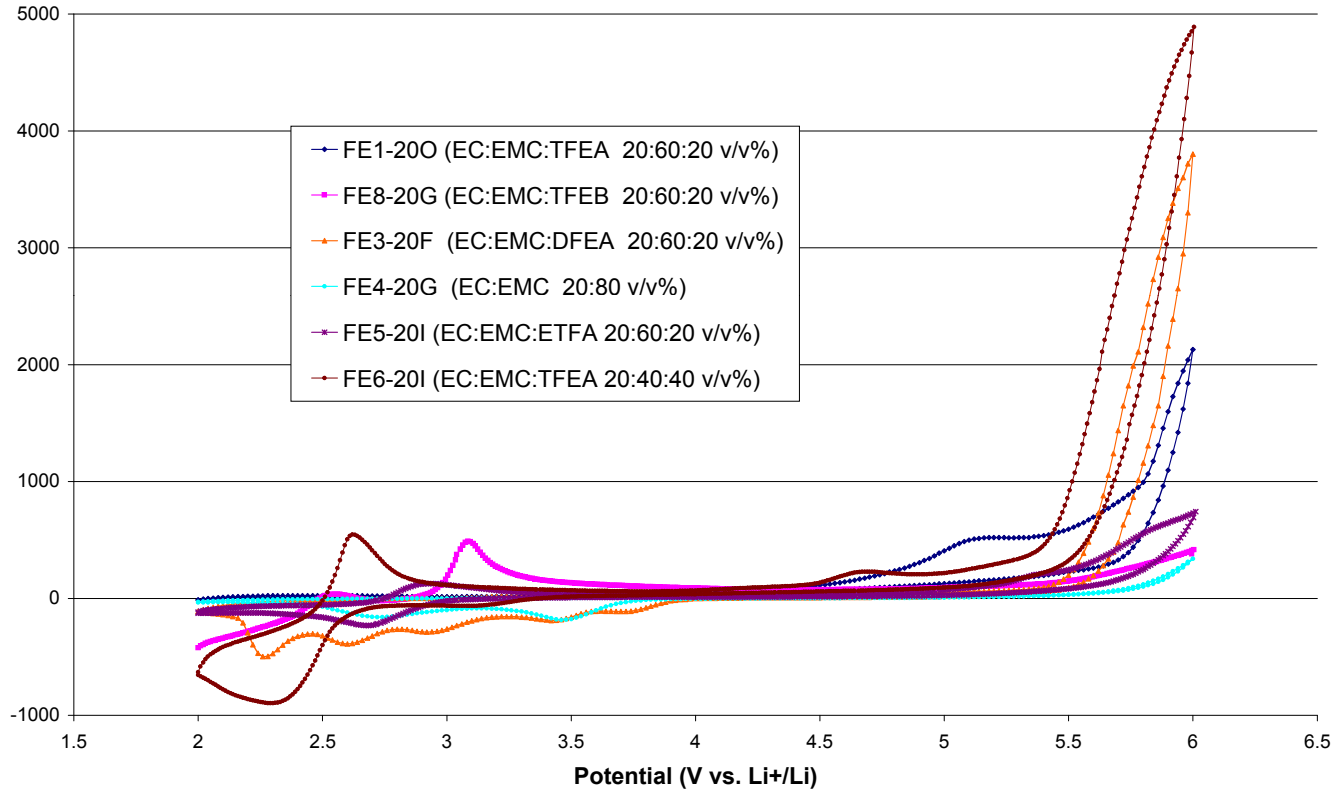
Development of Fluoroester Co-Solvent Containing Electrolytes

Electrolytes Selected for Evaluation in Experimental Cells

- **1.0 M $LiPF_6$ EC+EMC+TFEB (20:60:20 v/v %)**
- **1.0 M $LiPF_6$ EC+EMC+TFEB (20:40:40 v/v %)**
- **1.0 M $LiPF_6$ EC+EMC+TFEB (20:20:60 v/v %)**
- **1.0 M $LiPF_6$ EC+EMC+ETFA (20:60:20 v/v %)**
- **1.0 M $LiPF_6$ EC+EMC+TFEA (20:60:20 v/v %)**
- **1.0 M $LiPF_6$ EC+EMC+MPFP (20:60:20 v/v %)**

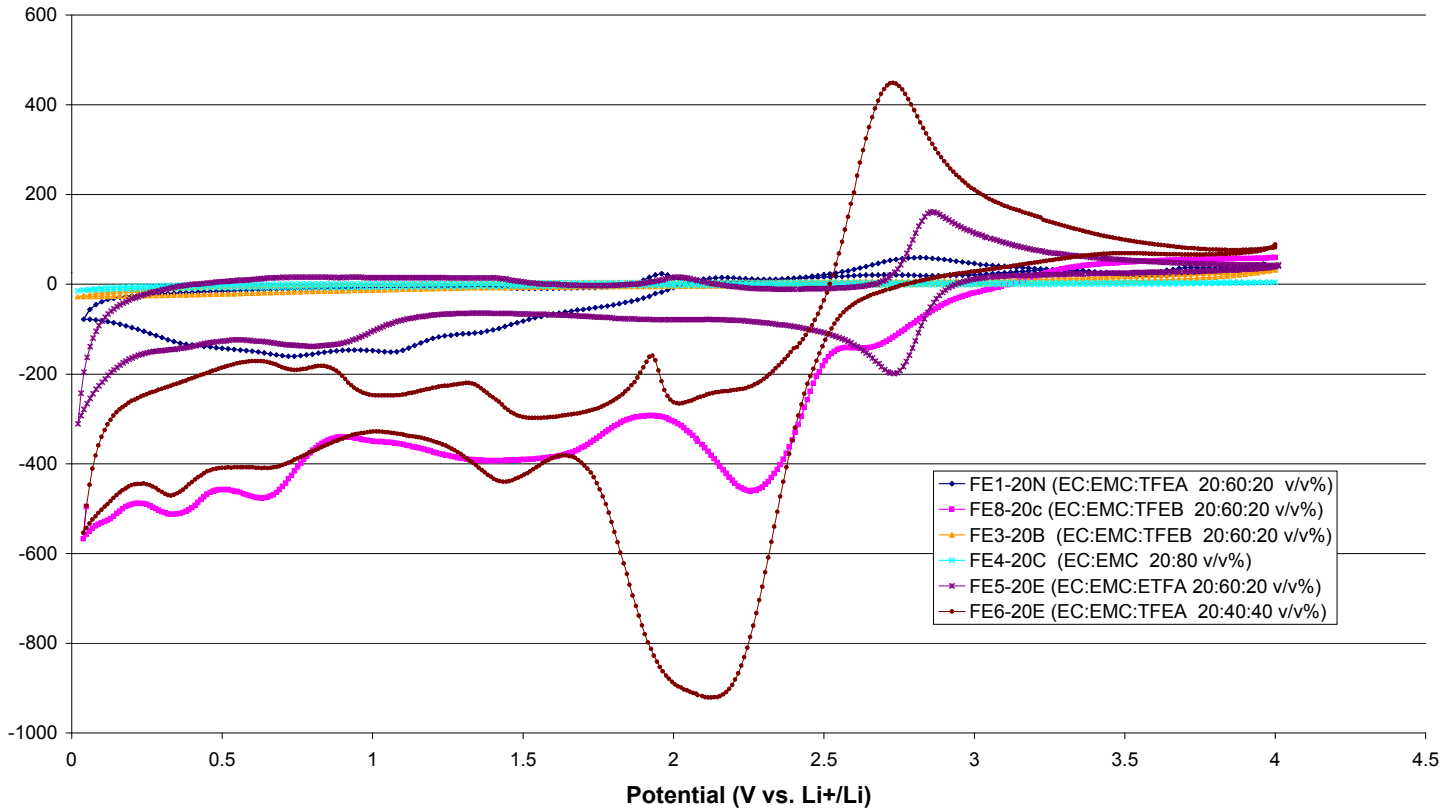
- Electrolytes were assessed in MCMB Carbon-$LiNiCoO_2$ glass wound (cylindrical) cells of 400-450 mAh size with Li metal reference electrodes.
- Performed assessment of performance (charge-discharge) at different rates and temperatures, high temperature resilience and detailed individual electrochemical kinetic measurements.
- These electrolytes provided a noticeable improvement in the low temperature performance (at -40°C or below) compared to baseline systems.

Determining Stability of Fluoroesters at High Potentials with Cyclic Voltammetry



- 1.0M $LiPF_6$ in electrolyte solution
- TFEB containing electrolyte demonstrates stability closest to the baseline material at higher potentials (>5.0V)

Determining Stability of Fluoroesters at Low Potentials with Cyclic Voltammetry



- 1.0M $LiPF_6$ in electrolyte solutions
- Multiple tests of TFEB containing electrolyte solutions give conflicting results

Evaluation of Fluoroester-Based Low Temperature Electrolytes: Formation Characteristics at 20ºC

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

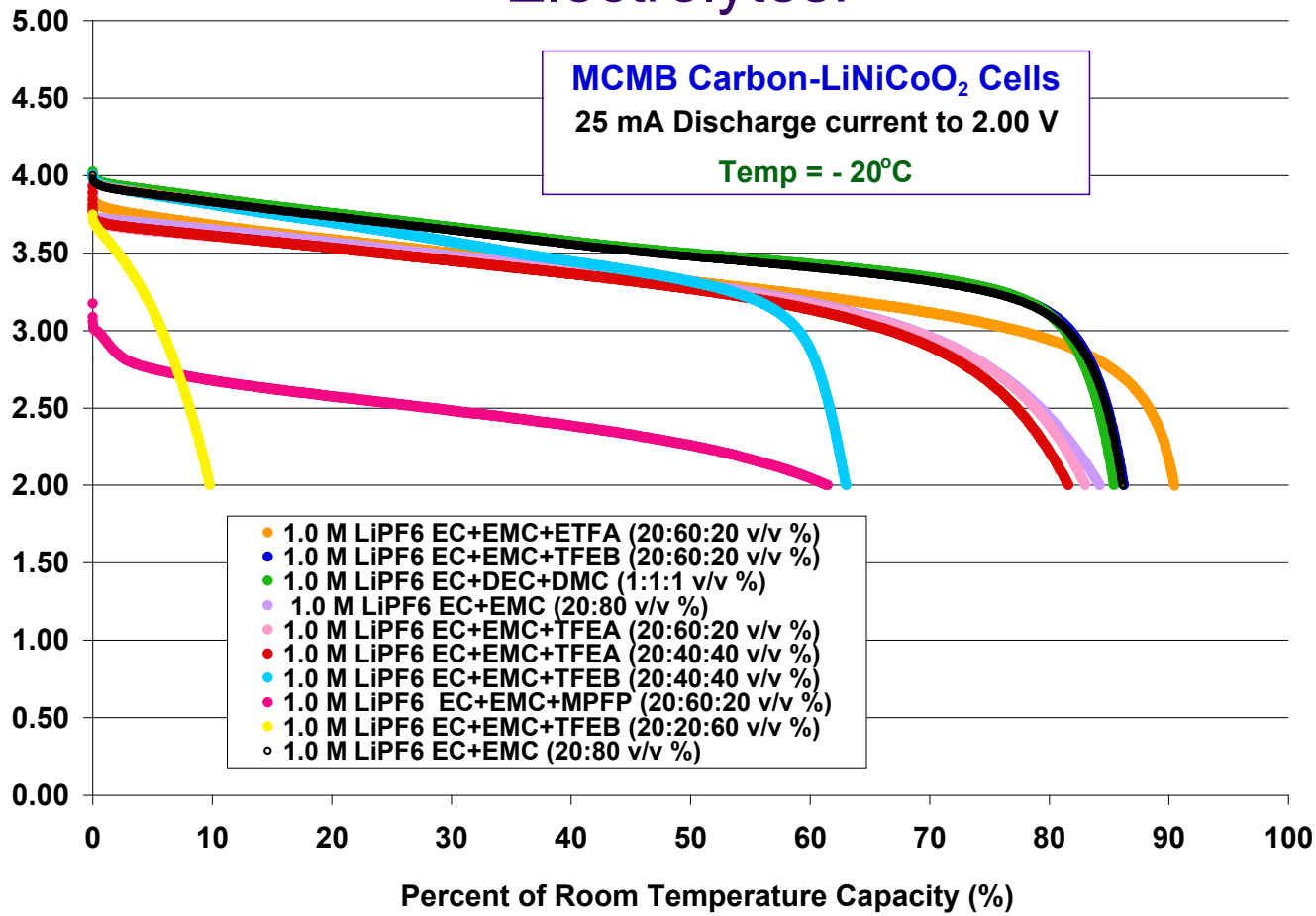
- The use of 2,2,2-trifluoroethyl butyrate as a co-solvent result in cells that display the highest coloumbic efficiency and low irreversible capacity loss.

Evaluation of Fluoroester-Based Low Temperature Electrolytes

Electrolyte Type →		1.0 M LiPF6 EC+EMC (10:90 v/v %)		1.0 M LiPF6 EC+EMC (20:80 v/v %)		1.0 M LiPF6 EC+EMC+TFEA (20:60:20 v/v %)		1.0 M LiPF6 EC+EMC+TFEA (20:40:40 v/v %)		1.0 M LiPF6 EC+EMC+TFEB (20:60:20 v/v %)		1.0 M LiPF6 EC+EMC+TFEB (20:40:40 v/v %)		1.0 M LiPF6 EC+EMC+TFEB (20:20:60 v/v %)		1.0 M LiPF6 EC+EMC+ETFA (20:60:20 v/v %)		1.0 M LiPF6 EC+EMC+MPFP (20:60:20 v/v %)	
Temperature	Current (mA)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)
23°C	25 mA	0.3679	100	0.3266	100	0.3035	100	0.3117	100	0.4312	100	0.4329	100	0.2862	100	0.3373	100	0.1884	100
- 20°C	25 mA	0.3052	82.96	0.2751	84.21	0.2519	83.02	0.2544	81.59	0.3718	86.23	0.2727	63.00	0.0280	9.79	0.3051	90.48	0.1158	61.44
	50 mA									0.3528	81.82	0.2314	53.45	0.0096	3.36	0.2764	81.97	0.0681	36.11
- 40°C	25 mA	0.2412	65.54	0.2023	61.93	0.1756	57.87	0.1657	53.17	0.3166	73.41	0.1064	24.57	0.0068	2.36	0.2580	76.49	0.0038	2.02
	50 mA			0.1217	37.27	0.0777	25.61	0.0518	16.61	0.2631	61.01	0.0364	8.40	0.0013	0.44	0.1983	58.79	0.0001	0.03
- 50°C	25 mA	0.1674	45.50	0.0736	22.54	0.0288	9.48	0.0208	6.66	0.2024	46.93	0.0347	8.02	0.0025	0.89	0.1221	28.31	0.0023	1.22
	50 mA									0.0324	7.52	0.0155	3.58	0.0000	0.01	0.0088	2.03	0.0000	0.01
- 60°C	5 mA	0.1957	53.20	0.1345	41.17	0.0633	20.88	0.0456	14.64	0.2723	63.14	0.1084	25.03	0.0057	1.99	0.1749	40.55	0.0000	0.02
	10mA	0.0620	16.84	0.0315	9.66	0.0091	2.99	0.0055	1.75	0.1918	44.47	0.0210	4.85	0.0016	0.56	0.0822	19.07	0.0000	0.00
	25 mA	0.0198	5.37	0.0021	0.65	0.0006	0.21	0.0002	0.08	0.0209	4.85	0.0080	1.84	0.0000	0.00	0.0018	0.41	0.0000	0.01
	50 mA			0.0001	0.04	0.0001	0.02	0.0000	0.01										

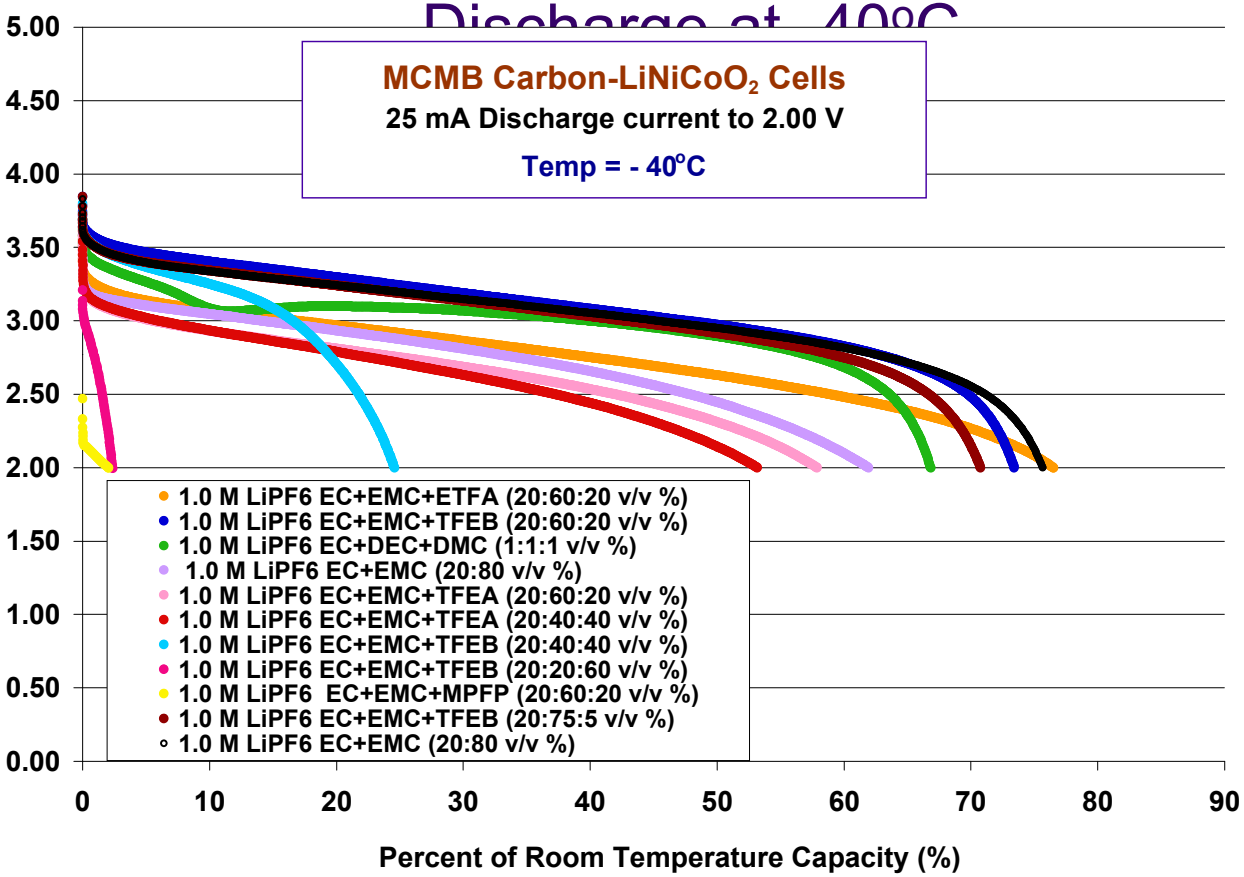
- 25 mA Discharge to 2.00 V (~ C/14 Discharge Rate)
- 10 mA Discharge to 2.00 V (~ C/35 Discharge Rate)
- Cells Charged at Room Temperature Prior To Discharge

Evaluation of Fluoroester-Based Low Temperature Electrolytes:



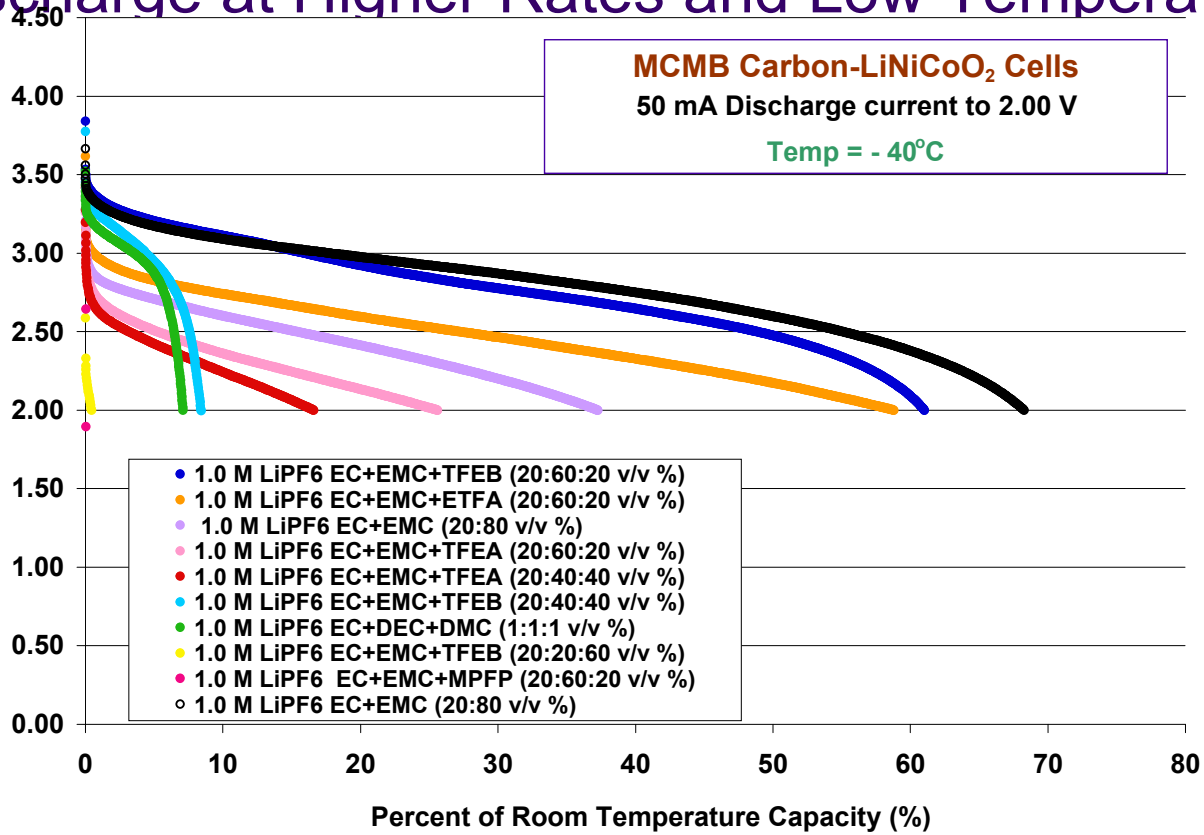
- Performance of fluoroester containing electrolyte solvents related to loadeing content
  - At -20, several fluoroester cells deliver performance close to baseline materials

Evaluation of Fluoroester-Based Low Temperature Electrolytes: Discharge at -40°C



- At depressed temperatures, greater variation in capacity values exists
- 20% solutions of ETFA and TFEB show best capacity retention, with values close to or exceeding baseline

Evaluation of Fluoroester-Based Low Temperature Electrolytes: Discharge at Higher Rates and Low Temperatures

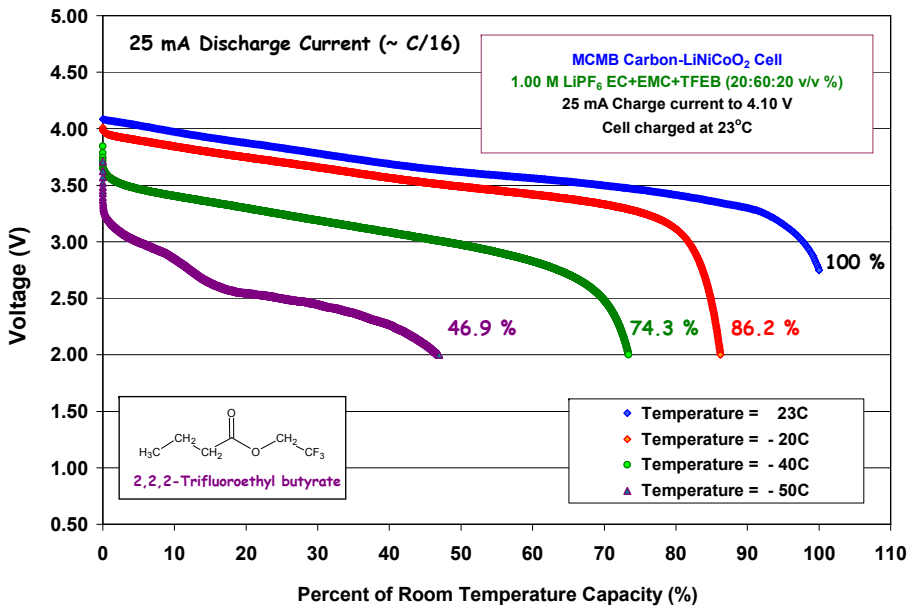


- Using higher discharge rates at –40°C, The cell containing the 1.0 M LiPF6 in EC+EMC+TFEB (20:60:20 v/v %) electrolyte again delivers superior performance at low temperature.

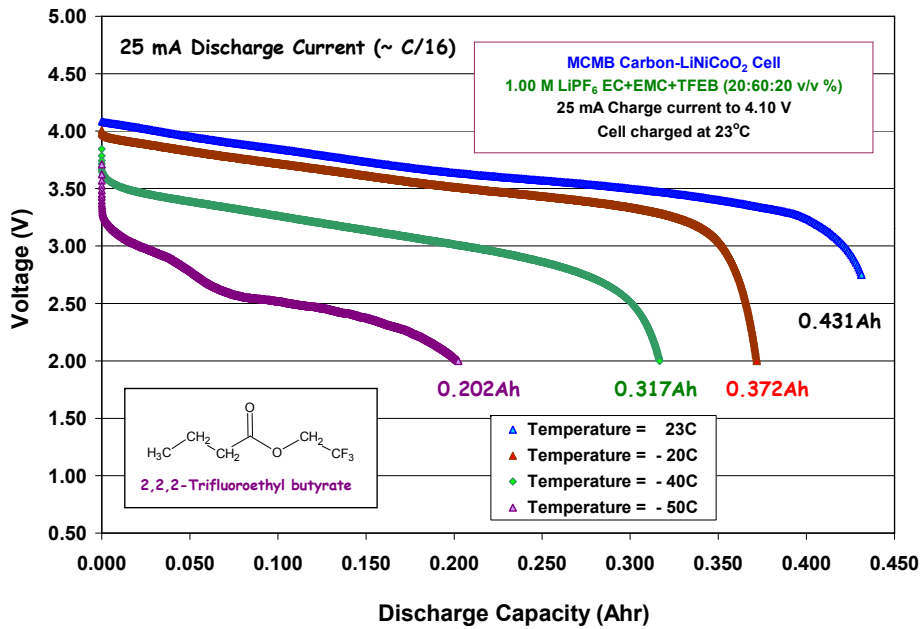
Evaluation of Fluoroester-Based Low Temperature Electrolytes

Discharge Characterization at Various Temperatures

Percent of Room Temperature Capacity



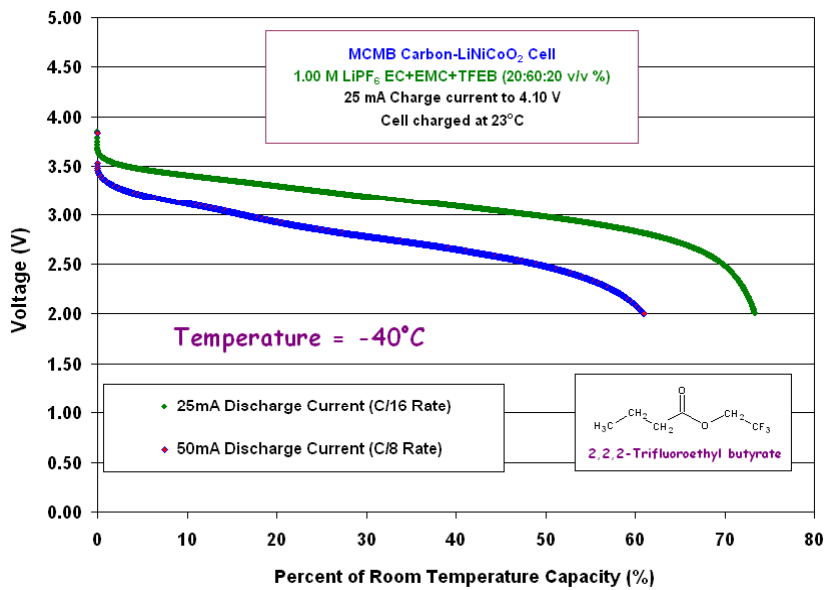
Discharge Capacity vs. Temperature



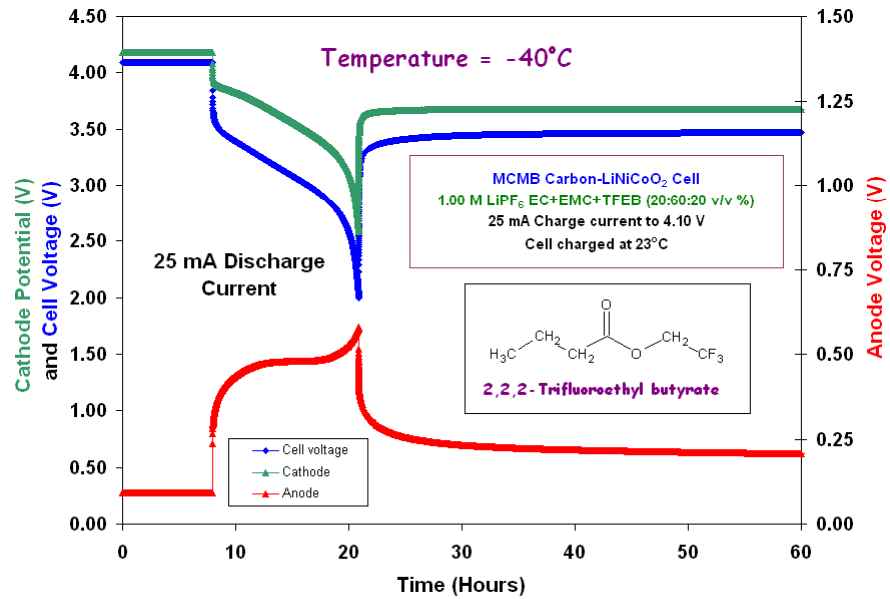
The cell containing the 1.0 M LiPF6 in EC+EMC+TFEB (20:60:20 v/v %) delivers excellent performance at –40°C delivering over 74% of the room temperature capacity.

Evaluation of Fluoroester-Based Low Temperature Electrolytes:
Cell Performance at –40°C (Charge at Room Temperature)

Percent of Room Temperature Capacity



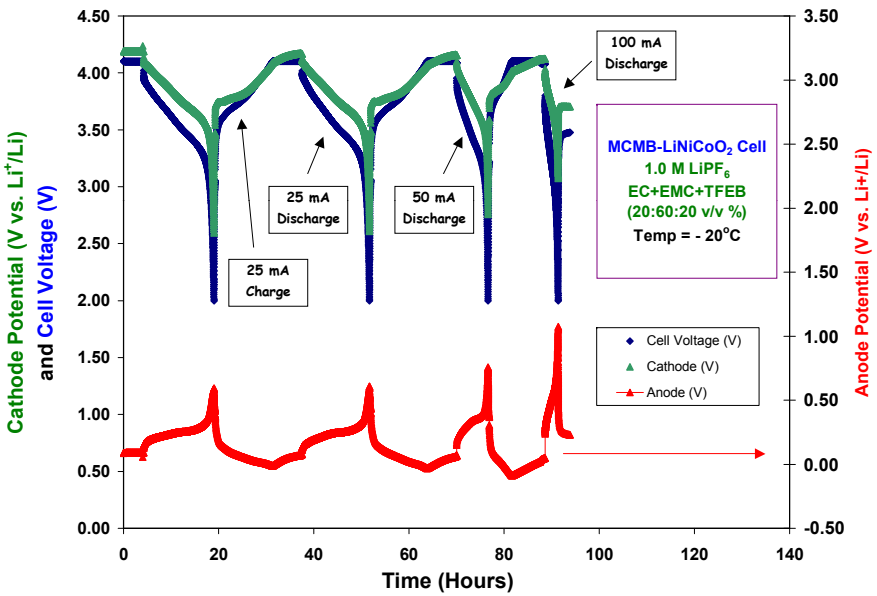
Electrode Behavior During Discharge



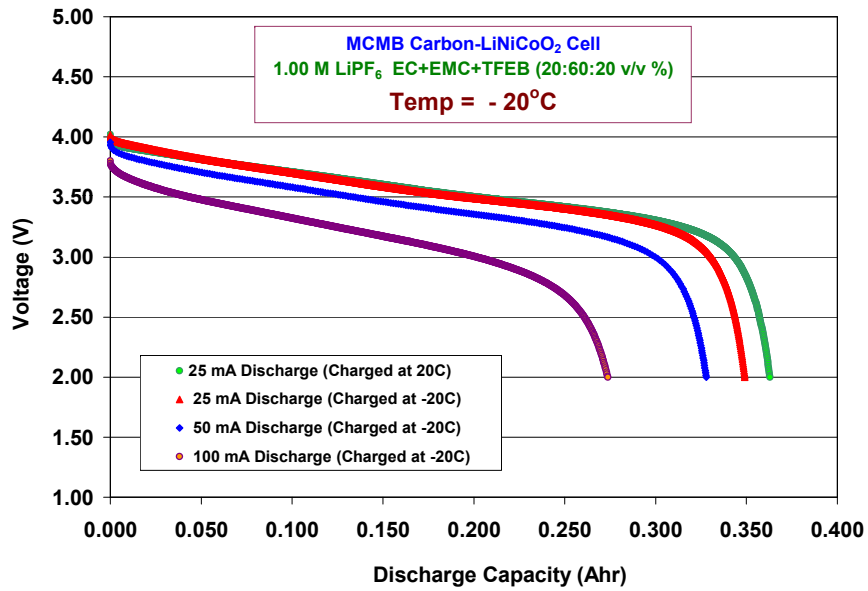
The cell containing the 1.0 M LiPF6 in EC+EMC+TFEB (20:60:20 v/v %) delivers excellent performance at –40°C delivering over 74% of the room temperature capacity, meeting program milestone.

Evaluation of Fluoroester-Based Low Temperature Electrolytes:
Cell Performance at –20°C (Charge at Low Temperature)

Overview of Rate Test at Low Temperature



Discharge Rate Capacity at –20°C

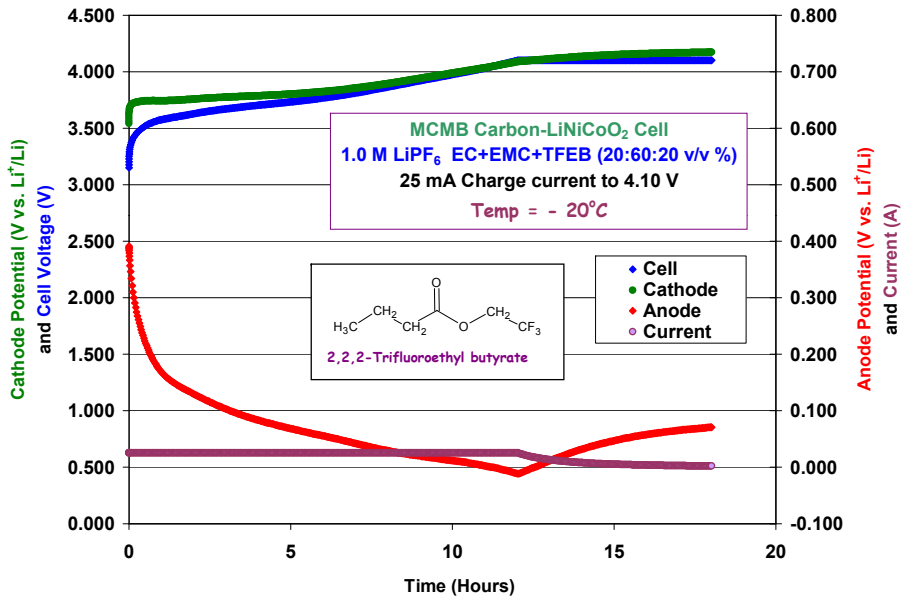


The cell containing the 1.0 M LiPF6 in EC+EMC+TFEB (20:60:20 v/v %) delivered excellent performance at –20°C when charged and discharged at low temperature, able to support C/4 discharge rates effectively with low temperature charging

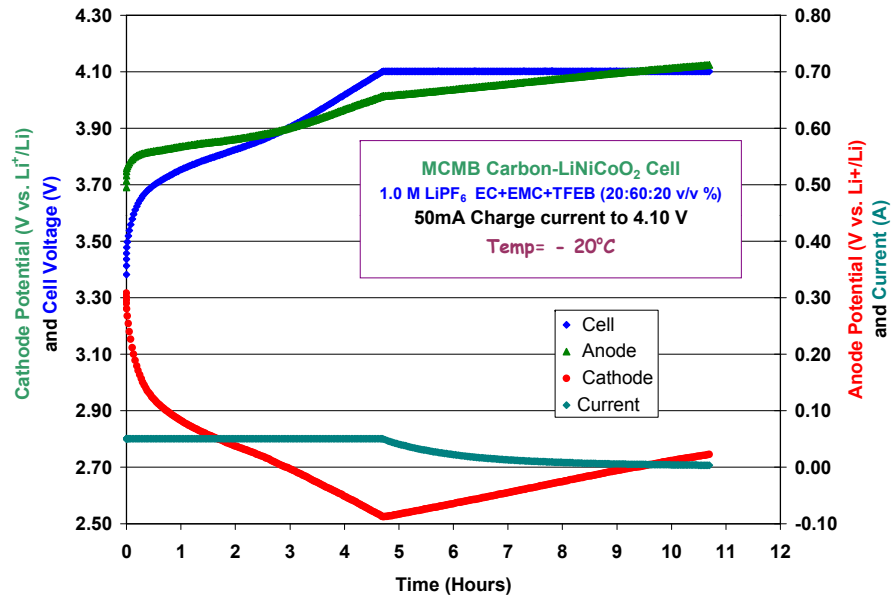
Milestone on Low Temperature (-40°C) Electrolyte

Evaluation of Fluoroester-Based Low Temperature Electrolytes
Cell Performance at –20°C (Charge at Low Temperature)

25 mA charge at –20°C



50 mA charge at –20°C



- As expected, the anode potential was driven more negative upon higher rate charge at low temperature (50 mA vs. 25 mA charging at –20°C).
- However, no pronounced lithium plating was observed (as determined by the voltage plateau on the subsequent discharge).

Tafel Polarization Measurements of MCMB and $LiNiCoO_2$ Electrodes

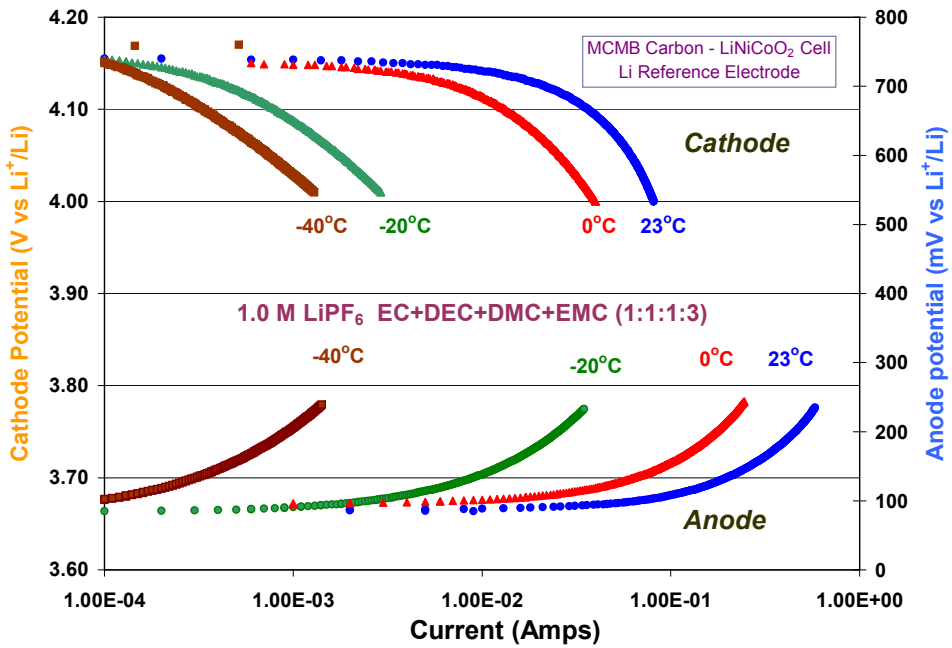
Effect of Electrolyte upon Polarization at Different Temperatures

- Tafel polarization measurements allow further insight into the kinetics of lithium intercalation/de-intercalation on MCMB anodes and $LiNiCoO_2$ 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.

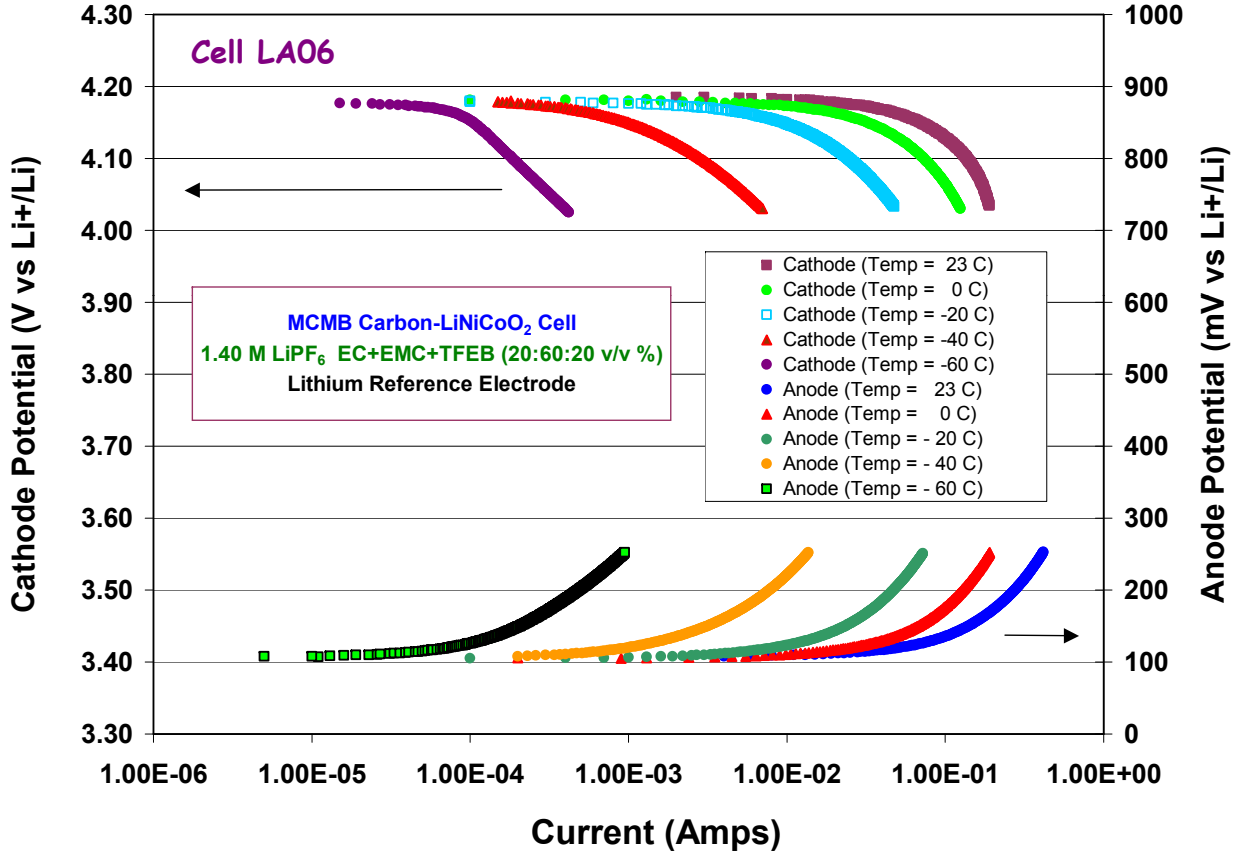
- Both anode and cathode polarization characteristics were measured at various different temperatures (23, 0, -20 and –40°C).



➢ In most cases, the cathode displays poorer kinetics and is performance limiting.

Milestone on Low Temperature (-40°C) Electrolyte

Evaluation of Fluoroester-Based Low Temperature Electrolytes

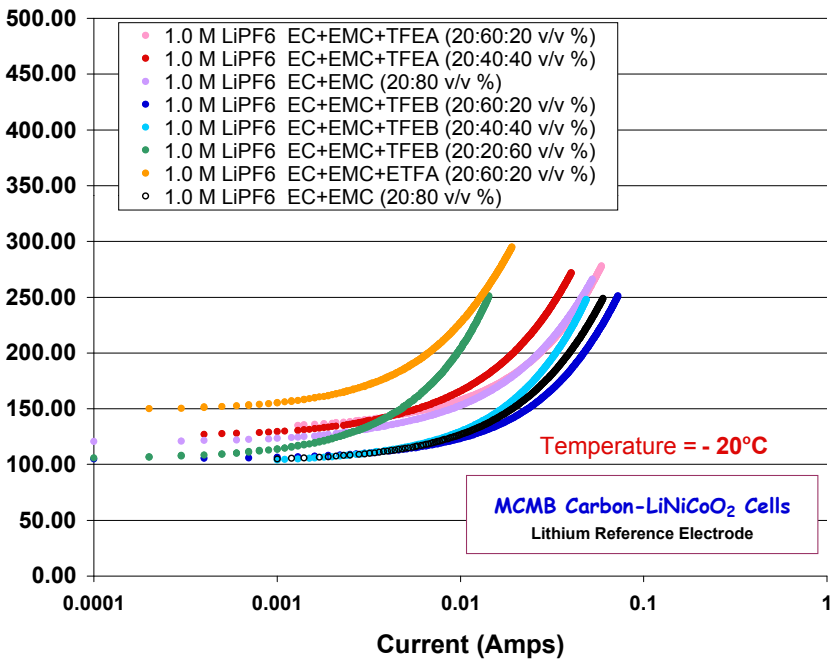


- **Kinetics were observed to be more favorable for the anode over the range of temperatures, representing desirable characteristics in terms of avoiding the possibility of lithium plating during low temperature charging.**

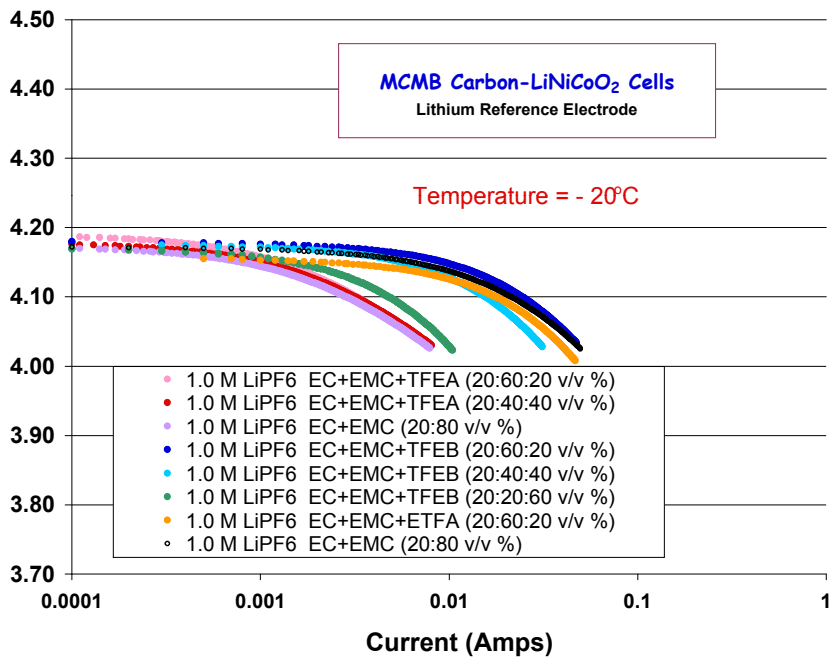
Milestone on Low Temperature (-40°C) Electrolyte

Evaluation of Fluoroester-Based Low Temperature Electrolytes
Tafel Polarization Measurements at -20°C

Anode Measurements at –20°C



Cathode Measurements at –20°C



- **The cell containing the trifluoroethyl butyrate electrolyte (1.0 M LiPF6 in EC+EMC+TFEB (20:60:20 v/v %) displayed superior kinetics at both the anode and the cathode at –20°C compared to the other electrolytes evaluated, suggesting good passivation characteristics and high conductivity.**

EIS Measurements of MCMB-$LiNiCoO_2$ Experimental Cells

EIS of SEI-Covered Carbon Electrodes

R_s : Electrolyte/Electrode Resistance

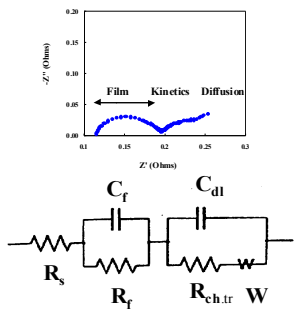
R_f : SEI Resistance

C_f : SEI Capacitance

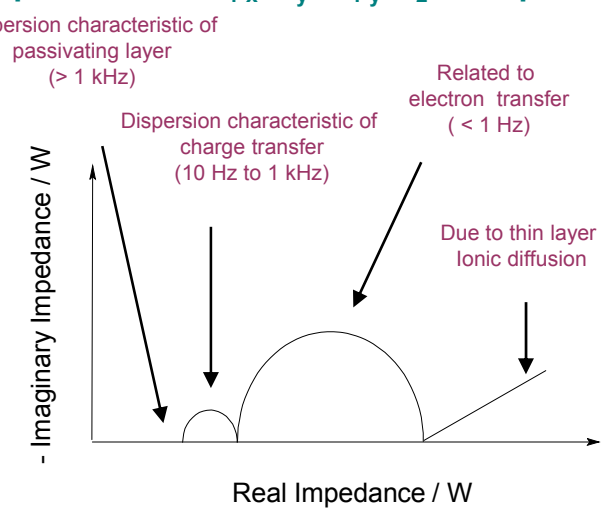
C_{dl} : Double layer Capacitance

$R_{ch.\,Tr}$: Charge Transfer Resistance

W : Diffusional (Warburg) Impedance

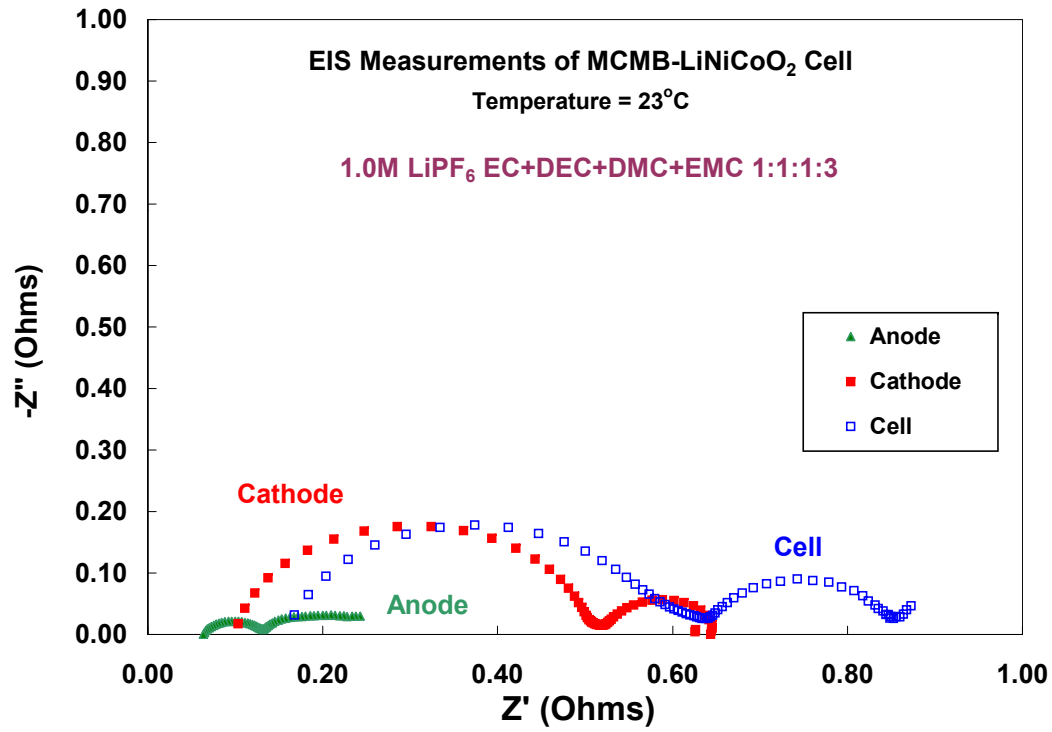


Interpretation of $Li_{1-x}Ni_yCo_{1-y}O_2$ EIS Spectra



EIS of MCMB-$LiNiCoO_2$ Cell

Low Temperature Electrolyte

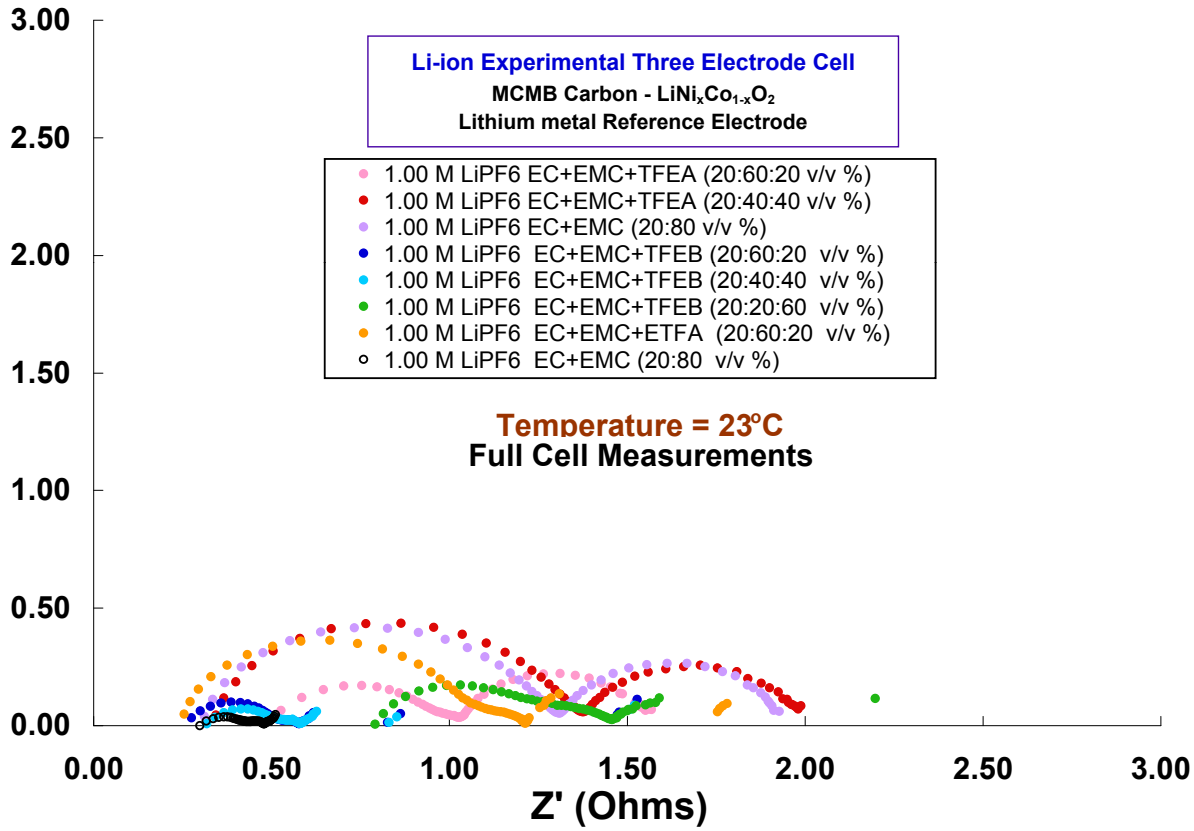


F. Nobili, R. Tossici, F. Croce, B. Scrosati, R. Marassi, *J. Power Sources*, **94**, *238-241* (2001).

EIS Measurements of MCMB-$LiNiCoO_2$ Experimental Cells

EIS of MCMB-$LiNiCoO_2$ Cells

Influence of Fluoroester Co-solvents upon Passivation Characteristics

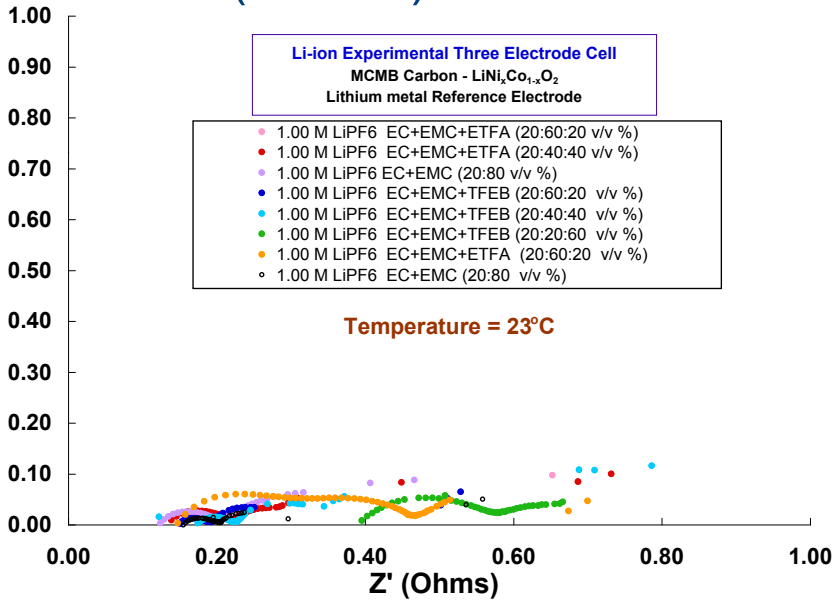


- In most cases, the fluoroester containing electrolytes resulted in decreased film and charge transfer resistances, suggesting desirable electrode passivation characteristics.

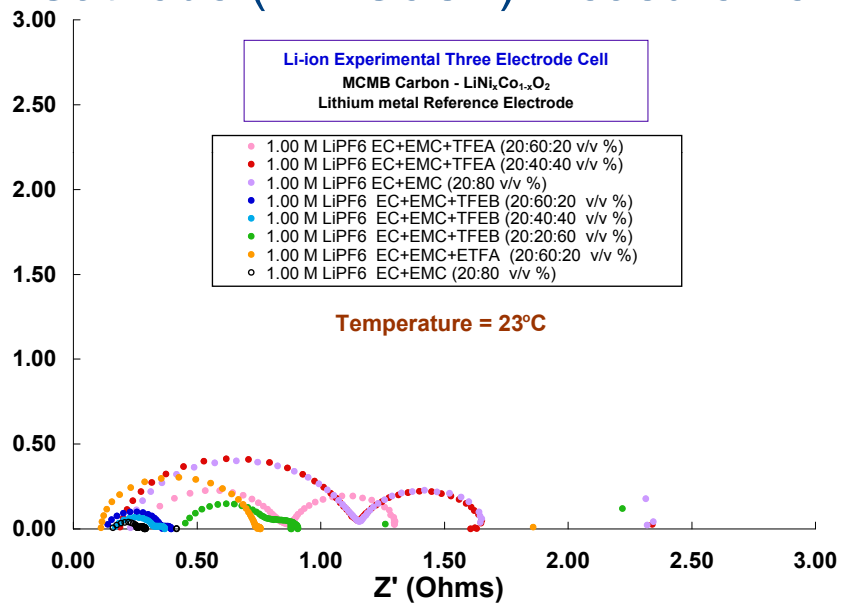
EIS Measurements of MCMB-$LiNiCoO_2$ Experimental Cells

Influence of Fluoroester Co-solvents upon Passivation Characteristics

Anode (MCMB) Measurements



Cathode (LiNiCoO2) Measurements



- **Although the addition of fluoroester co-solvents was primarily envisioned to affect the filming process at the anode, a substantial desirable influence was also observed at the cathode.**

SUMMARY and CONCLUSIONS

- *Use of fluorinated ester co-solvents in Li-ion electrolytes*
  - *A number of partially fluorinated ester co-solvents have been blended into multi-component electrolytes and have been observed to result in enhanced performance,especially at low temperatures, in experimental MCMB-$LiNiCoO_2$ cells.*
  - *The most promising co-solvent evaluated was 2,2,2-trifluoroethyl butyrate (TFEB) which has outperformed the baseline all carbonate mixtures.*
- *Future Work*
  - *Effort will be devoted to further optimizing fluorinated carbonate and ester-containing electrolyte to provide improved operational temperature range and safety.*
  - *Promising electrolytes will be incorporated into large capacity prototype cells.*

Acknowledgments

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