

FINAL REPORT
FOR CRADA NO. C-05-15
BETWEEN
BROOKHAVEN SCIENCE ASSOCIATES
AND
MER CORPORATION

Project Entitled: New Electrolytes and Electrolyte Additives to Improve the Low Temperature Performance of Lithium-ion Batteries

Brookhaven PI: Xiao-Qing Yang

Submitted by: Michael J. Furey
Manager, Research Partnerships
Brookhaven National Laboratory

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Report for CRADA with MER Corporation (CRADA No. BNL-C-05-15)

Proposal Title: New electrolytes and electrolyte additives to improve the low temperature performance of lithium-ion batteries

Laboratory P.I.(s) Dr. Xiao-Qing yang, Chemistry Department, BNL.
Phone: (631) 344-3663, Fax: (631) 344-5815, E-mail: xyang@bnl.gov

Budget \$283,300

Project Duration: Three years.

Technical Abstract:

In this program, two different approaches were undertaken to improve the role of electrolyte at low temperature performance – through the improvement in (i) ionic conductivity and (ii) interfacial behavior. Several different types of electrolytes were prepared to examine the feasibility of using these new electrolytes in rechargeable lithium-ion cells in the temperature range of +40°C to -40°C. The feasibility studies include (a) conductivity measurements of the electrolytes, (b) impedance measurements of lithium-ion cells using the screened electrolytes with different electrochemical history such as [(i) fresh cells prior to formation cycles, (ii) after first charge, and (iii) after first discharge], (c) electrical performance of the cells at room temperatures, and (d) charge discharge behavior at various low temperatures.

Among the different types of electrolytes investigated in Phase I and Phase II of this SBIR project, carbonate-based LiPF₆ electrolytes with the proposed additives and the low viscous ester as a third component to the carbonate-based LiPF₆ electrolytes show promising results at low temperatures. The latter electrolytes deliver over 80% of room temperature capacity at -20 °C when the lithium-ion cells containing these electrolytes were charged at -20 °C. Also, there was no lithium plating when the lithium-ion cells using C-C composite anode and LiPF₆ in EC/EMC/MP electrolyte were charged at -20 °C at C/5 rate. The studies of ionic conductivity and AC impedance of these new electrolytes, as well as the charge discharge characteristics of lithium-ion cells using these new electrolytes at various low temperatures provide new findings: The reduced capacity and power capability, as well as the problem of lithium plating at low temperatures charging of lithium-ion cells are primarily due to slow the lithium-ion intercalation/de-intercalation kinetics in the carbon structure.

Technical Report:

Nine fluorinated lithium phenyldifluoroborane compounds were synthesized at Brookhaven National Lab (BNL), the subcontractor of this program and their ionic conductivities and electrochemical characteristics in DME and EC/DME (1/2 volume ratio) solvents are compared with those of lithium tetrafluoroborate salt. The starting materials were purchased from Aldrich Chemical Co. except 2,5-bis(trifluoromethyl)phenylboronic acid which was designed and synthesized at BNL. All the reactions and processes, which are sensitive to moisture, were performed under argon atmosphere. Proton NMR spectra were recorded on a Hitachi R-1200 (60 MHz) spectrometer. The synthesis procedures for the series of fluorinated potassium phenyltrifluoroborate (1) are described in previous literatures [3, 4]. For the series of fluorinated phenyldifluoroborane (2), we follow the procedures modified from those previously reported [4], which are outlined as follows: 0.05~0.1M of fluorinated potassium phenyltrifluoroborate synthesized in step (1) was added to 150 ml of fluorotrichloromethane to make suspension. The prepared suspension solution was cooled with acetone and dry ice, followed by bubbling of boron trifluoride into the solution with stirring until it saturates, which usually takes 1 to 1.5h. The solution was left to warm up to room temperature with continuous stirring for another 2h. Precipitates were separated by centrifugation followed by evaporation to obtain the pure borane. Table II show the boiling temperatures and yields during synthesis procedures of each borane precursors.

The general procedures for the synthesis of step (3), lithium fluorinated phenyltrifluoroborate are as follows:

0.05M lithium fluoride was added into 15~20 ml of anhydrous 1,2-dimethoxyethane (DME). The mixture was cooled in ice bath. Fluorinated phenyldifluoroborane was added into the mixture and stirred at room temperature for 2~3 hours, followed by filtration of un-reacted lithium fluoride. The solvent was evaporated and the liquid residue was sublimed at 60°C/0.2mm-Hg. Then, obtained solids were re-crystallized in ether or ether-pentane. These products contain both crystalline ether and DME. The ether can be removed at 50~60°C/0.2mm-Hg, while the removal of DME requires higher temperature. However, mono or difluorinated phenyltrifluoroborate will decompose at higher temperature. Although using ether as solvent has the advantage of no co-crystallized solvent, it gives lower yield of the final products.

The followings are the outlines of the synthesis procedures for each of the final compounds, which are lithium fluorinated phenyldifluoroborane salts:

Lithium phenyltrifluoroborate: The crude product was obtained from reacting 5g (0.04M) of phenyldifluoroborane with 1.04g of lithium fluoride for one day at room temperature followed by drying for 3h at 60°C. The crude product was purified by re-crystallization in ether to give 4.8g of needle-shaped crystal. The final product was obtained by drying at 50°C/0.3mm-Hg for 3h. NMR spectra showed that the final product contained ½ mole of crystalline DME. ¹H NMR (Acetone-d₆) δ: 3.3 (s, 3H), 3.6 (s, 2H), 7~7.3 (m, 3H), 7.3~7.7 (m, 2H) ppm.

Lithium 2-fluorophenyltrifluoroborate: The sample synthesis procedures are

basically the same with those of lithium phenyltrifluoroborate. 3.3g of 2-fluorophenyldifluoroborane were reacted with 0.6g of lithium fluoride in 10 ml of DME at room temperature for 2 days to obtain the crude product. Then, the crude product was purified by re-crystallization in a mixed solvent of ether-pentane to obtain needle-shaped crystal, followed by drying at 50°C/0.1mm-Hg for 3h. The yield was 3.7g. NMR spectra showed that the final product contained ½ mole of crystalline DME. ¹HNMR (Acetone-d₆) δ: 3.3 (s, 3H), 3.6 (s, 2H), 6.75~7.35 (m, 3H), 7.35~8.2 (m, 1H) ppm.

Lithium 3, 5-difluorophenyltrifluoroborate: 6.5g of 3,5-difluorophenyldifluoroborane were reacted with 1.04g of lithium fluoride for 2h at room temperature. The crude product was purified by recrystallization in a mixed solvent of ether-pentane to obtain pure crystal, followed by drying at 65°C/0.15mm-Hg for 1h. The yield was 5g. NMR spectra showed that the final product contained ½ mole of crystalline DME. ¹HNMR (Acetone-d₆) δ: 3.3 (s, 3H), 3.6 (s, 2H), 6.35~6.9 (m, 1H), 6.9~7.25 (m, 2H) ppm.

Lithium 2-trifluoromethylphenyl trifluoroborate: 9.7g (0.05M) of 2-trifluoromethyldifluoroborane were reacted with 1.3g of lithium fluoride for 15h at room temperature. The crude product was recrystallized in ether-pentane to give pure plate-shaped crystal, followed by drying at 50°C/0.15mm-Hg for 1h. The yield was 12.5g. It contained 1 mole of crystalline DME. ¹HNMR (Acetone-d₆) δ: 3.3 (s, 6H), 3.6 (s, 4H), 7.2~7.7 (m, 3H), 7.7~8 (m, 1H) ppm.

Lithium 2, 5-bis(trifluoromethyl)phenyltrifluoroborate: 11.5g of 2,5-bis(trifluoromethyl)phenyldifluoroborane were reacted with 1.14g of lithium fluoride for 2h at room temperature. The crude product was purified by recrystallization in ether-pentane to give 10g of pure product, followed by drying at 50°C/0.3mm-Hg for 2h. It contained 1 mole of crystalline DME. ¹HNMR (Acetone-d₆) δ: 3.3 (s, 6H), 3.6 (s, 4H), 7.6~7.8 (m, 2H), 8~8.3 (m, 1H) ppm.

Lithium 3, 5-bis(trifluoromethyl)phenyltrifluoroborate: 8.12g of 3,5-bis(trifluoromethyl)phenyldifluoroborane were reacted with 0.8g of lithium fluoride to give 8g of needle-shaped crystal, followed by drying at 65°C/0.15mm-Hg for 2h. It contained ½ mole of crystalline DME. ¹HNMR (Acetone-d₆) δ: 3.3 (s, 3H), 3.6 (s, 2H), 7.85 (s, 1H), 8.05 (s, 2H) ppm.

**Table I: Boiling Temperatures and Yields
During Synthesis of Borane Precursors**

Borane	Boiling Temperature (°C)	Yield (%)
Phenyldifluoroborane	96~97	68
2-Fluorophenyldifluoroborane	110~112	41
3,5-Difluorophenyldifluoroborane	95~97	52
2-Trifluoromethylphenyldifluoroborane	124~126	95
2,5-Bis(trifluoromethyl)phenyldifluoroborane	130~132	84
3,5-Bis(trifluoromethyl)phenyldifluoroborane	120~122	80

2,5,6-Trifluorophenyldifluoroborane	118~120	57
2,3,5,6-Tetrafluorophenyldifluoroborane	113~115	48
Pentafluorophenyldifluoroborane	108~110	57

Lithium 2,5,6-trifluorophenyltrifluoroborate: 8g of 2,5,6-trifluorophenyldifluoroborane were reacted with 1.17g of lithium fluoride for 3h at room temperature to give 6.4g of pure product, followed by drying at 100°C/0.2mm-Hg for 8h. It contained no crystalline DME. ¹HNMR (Acetone-d₆) δ: 6.5~7.5 (m) ppm.

Lithium 2,3,5,6-tetrafluorophenyltrifluoroborate: 5.54g of 2,3,5,6-tetrafluorophenyldifluoroborane were reacted with 0.73g of lithium fluoride to give 4.5g of plate-shaped crystal, followed by drying at 100°C/0.15mm-Hg for 7h. It contained no crystalline DME. Melting point was greater than 350°C. ¹HNMR (Acetone-d₆) δ: 6.8~7.4 (m) ppm.

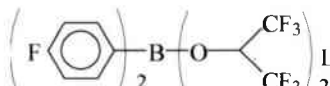
Lithium pentafluorophenyltrifluoroborate: 13g of pentafluorophenyldifluoroborane were reacted with 1.56g of lithium fluoride to give 7.8g needle-shaped crystals, followed by drying at 100°C/0.15mm-Hg for 7h. It contained no crystalline DME. Melting point was greater than 350°C.

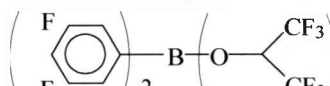
Several electrolytes were prepared at Brookhaven National Lab (BNL). These electrolytes were shipped to MER for investigation towards possible low temperature applications in lithium-ion batteries. The compositions of the eight electrolytes are shown below:

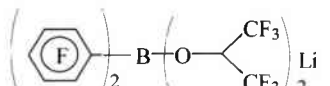
Sample #**Electrolyte Composition**

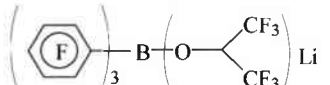
19-60-1 1.0 M LiPF₆ in EC/ N-Methyl-oxazolidinone (1:10)

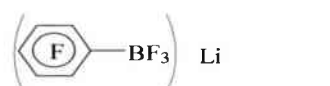
19-60-2 1.0 M LiPF₆ in EC/ N-Methyl-oxazolidinone (1:15).

19-60-3 0.6M  with Et₂O in EC/EMC (1:10)

19-60-4 0.6M  in EC/EMC (1:10)

19-60-5 0.6M  with Et₂O in EC/EMC (1:10)

19-60-6 0.6M  with Et₂O in EC/EMC (1:10)

19-60-7 0.6M  in EC/EMC (1:10)

19-60-8	0.6M LiBF_4	in EC/EMC (1:10)
20-14-1	1.0 M LiPF_6 in EC/ N-Methyl-oxazolidinone (1:20, v/v)	
20-14-2	0.6 M $(\text{C}_6\text{F}_5)_2\text{B}[(\text{CF}_3)_2\text{CHO}]_2\text{Li}$ with Et_2O in EC/ N-Methyl-oxazolidinone (1:20, v/v).	
20-50-1	1.0 M LiPF_6 in EC/N-Methyl Oxazolidinone (1:8, v/v)	
20-50-2	1.0 M LiPF_6 in EC/N-Methyl Oxazolidinone (1:5, v/v)	
20-58-1	1.0 M LiPF_6 in EC/EMC/Methyl cyclopropane carboxylate (1:1:8, v/v)	
20-58-2	1.0 M LiPF_6 in EC/EMC/Methyl cyclopentane carboxylate (1:1:8, v/v)	

Samples 19-60-1 and 19-60-2 are electrolytes in new solvent with different concentrations of EC. Samples 19-60-3 to 19-60-7 are electrolytes with five new boron salts, where -3, -5, and -6 has crystallized in $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ noted as Et_2O . 19-60-8 is LiBF_4 salt as reference. -3 to -8 samples are all in 0.6M EC/EMC since this concentration has the highest conductivity and can make more solutions with limited amount of sample.

Samples 20-14-1, 20-14-2, 20-50-1, and 20-50-2 are electrolytes with different proportions of EC/NMO than those investigated in the last reporting period. Samples 20-58-1 and 20-58-2 are LiPF_6 -based electrolytes in two new cyclic ester solvents.

Conductivity measurements were performed by BNL scientists at 25°C using a Hewlett-Packard 4129A Impedance Analyzer in the frequency range from 5Hz to 10 MHz. Cells with Pt electrodes were used for the measurements. The cell constants were calibrated by measuring a 0.05N KCl standard aqueous solution. The ionic conductivities of DME and EC/DMC solutions containing various boron based lithium salts at four different concentrations (0.4M, 0.6M, 0.8M, 1.0M) in comparison with the reference LiBF_4 salt are listed in Table III. The electrolyte contains the salt with fully fluorinated phenyl ring $((\text{C}_6\text{F}_5)\text{BF}_3\text{Li})$ resulted in the highest conductivity. This salt was selected for low temperature conductivity studies and sent to MER Corp. for cyclability studies at different temperatures. The ionic conductivities at different temperatures of this new salt in comparison with LiPF_6 and LiBF_4 are listed in Table IV. It can be seen that the ionic conductivity of the new boron based salt, $(\text{C}_6\text{F}_5)\text{BF}_3\text{Li}$, is lower than LiPF_6 , but very close to LiBF_4 salt.

Table II: Ionic Conductivity of Fluorinated Lithium Phenyltrifluoroborates

	Solvents	Concentration of Lithium Salts			
		0.4M	0.6M	0.8M	1.0M
1. (C ₆ H ₅)BF ₃ Li·½DME	DME	4.68×10 ⁻⁴	9.89×10 ⁻⁴	1.50×10 ⁻³	1.95×10 ⁻³
	EC/DMC*	2.29×10 ⁻³	2.60×10 ⁻³	2.76×10 ⁻³	2.60×10 ⁻³
2. (C ₆ H ₄ F)BF ₃ Li·½DME	DME	5.87×10 ⁻⁴	1.13×10 ⁻³	1.64×10 ⁻³	2.10×10 ⁻³
	EC/DMC*	2.66×10 ⁻³	3.0×10 ⁻³	3.04×10 ⁻³	3.0×10 ⁻³
3. (C ₆ H ₃ F ₂)BF ₃ Li·½DME	DME	9.86×10 ⁻⁴	1.80×10 ⁻³	2.57×10 ⁻³	3.17×10 ⁻³
	EC/DMC*	2.83×10 ⁻³	3.22×10 ⁻³	3.40×10 ⁻³	3.45×10 ⁻³
4. (C ₇ H ₄ F ₃)BF ₃ Li·DME	DME	4.67×10 ⁻⁴	9.20×10 ⁻⁴	1.40×10 ⁻³	1.76×10 ⁻³
	EC/DMC*	2.54×10 ⁻³	2.88×10 ⁻³	2.98×10 ⁻³	2.91×10 ⁻³
5. (C ₈ H ₃ F ₆)BF ₃ Li·DME	DME	1.04×10 ⁻³	1.77×10 ⁻³	2.58×10 ⁻³	2.94×10 ⁻³
	EC/DMC*	2.98×10 ⁻³	3.30×10 ⁻³	3.28×10 ⁻³	3.10×10 ⁻³
6. (C ₈ H ₃ F ₆)BF ₃ Li·½DME	DME	1.74×10 ⁻³	2.93×10 ⁻³	3.23×10 ⁻³	3.73×10 ⁻³
	EC/DMC*	2.87×10 ⁻³	3.20×10 ⁻³	3.32×10 ⁻³	3.28×10 ⁻³
7. (C ₆ H ₂ F ₃)BF ₃ Li	DME	9.89×10 ⁻⁴	1.90×10 ⁻³	2.74×10 ⁻³	3.38×10 ⁻³
	EC/DMC*	3.48×10 ⁻³	3.80×10 ⁻³	3.80×10 ⁻³	3.54×10 ⁻³
8. (C ₆ H ₄ F ₄)BF ₃ Li	DME	1.31×10 ⁻³	2.39×10 ⁻³	3.32×10 ⁻³	4.0×10 ⁻³
	EC/DMC*	3.84×10 ⁻³	4.11×10 ⁻³	4.16×10 ⁻³	4.01×10 ⁻³
9. (C ₆ F ₅)BF ₃ Li	DME	2.26×10 ⁻³	3.90×10 ⁻³	5.0×10 ⁻³	5.63×10 ⁻³
	EC/DMC*	4.48×10 ⁻³	4.95×10 ⁻³	4.94×10 ⁻³	4.65×10 ⁻³
10. LiBF ₄	DME	1.04×10 ⁻³	2.09×10 ⁻³	3.19×10 ⁻³	4.33×10 ⁻³
	EC/DMC*	4.25×10 ⁻³	4.88×10 ⁻³	5.18×10 ⁻³	5.16×10 ⁻³

EC/DMC = 1/2 Volume

Table III: Ionic Conductivity of 1 M (C₆F₅)BF₃Li, LiBF₄, and LiPF₆ at Different Temperatures

#	salt	BL	DM C	NMO	Conductivit y (mS/cm) 25 °C	Conductivit y (mS/cm) -20 °C	Conductivit y (mS/cm) -40 °C	Conductivit y (mS/cm) -60 °C	Conductivit y (mS/cm) -80 °C
1	BLi	7	1	1	7.23	2.41	1.05	0.288	0.0976
2	BF ₄	7	1	1	7.69	3.19	1.59	0.340	0.215
3	PF ₆	7	1	1	11.7	3.84	1.76	0.450	0.154
6	PF ₆			1	31.8	18.5	12.4	6.99	3.13

BLi is $(C_6F_5)BF_3Li$ salt; The number for the solvent means the volume ratio

NMO is N-methyloxazolidinone

BL is Butyrolactone

The ionic conductivities of the different electrolytes measured at different temperatures during this reporting period are shown in Table V. The ionic conductivities of the two samples 19-60-1 and 19-60-2 were made with $LiPF_6$ salt in a mixture of ethylene carbonate and N-methyl oxazolidinone in the proportions of 1:10 (v/v) and 1:15 (v/v), respectively, and were reported in the last Continuation Application/Progress Report are also shown in the Table for comparison.

**Table IV: Ionic Conductivity of the Electrolytes
at Different Low Temperatures**

Sample	Conductivity (mS/cm)				
	25°C	-20°C	-40°C	-60°C	-80°C
19-60-1	27.5	15.0	9.80	5.10	2.0
19-60-2	28.6	16.4	10.6	5.50	2.3
19-60-3	6.3				
19-60-4	5.6				
19-60-5	5.6				
19-60-6	5.3				
19-60-7	4.6				
19-60-8	4.9				
20-14-1	29.6	17.0	11.2	5.92	2.54
20-14-2	5.33	2.25	0.982	0.512	0.227
20-50-1	26.2	13.8	9.36	4.98	1.86
20-50-2	25.2	12.4	8.82	4.88	1.62
20-58-1					
20-58-2					

These Electrolytes shown good ionic conductivity at low temperatures.

Significant problems: No significant problems were encountered during this CRADA. Most of the problems were quickly resolved by effective communication between the two research groups at BNL and MER.

Industry benefits realized: The industrial partner, MER Corporation, benefited a lot from the organic synthesis expertise at BNL. The new salts for the low temperature electrolytes synthesized at BNL were one of the key components of the success of their phase I and phase II STTR projects awarded by US DOE. MER was awarded a new SBIR phase I project from OSD. MER has signed a new CRADA agreement with BNL for synthesizing new high voltage electrolytes for lithium batteries.

Laboratory benefits realized: BNL team benefited from the industrial expertise of MER in testing the newly developed electrolytes in operating lithium battery cells at different temperatures and various charge-discharge cycling conditions. These testing results will help the BNL team to modify and redesign the structures of the new salt and electrolyte systems for lithium batteries, which is quite important for the core DOE funded projects the BNL battery team are carrying out.

Follow up work: The follow up work will be worked out through the new CRADA with MER.