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Dinitrile-based Electrolytes for high voltage Lithium-Ion Batteries

Nuha Salem, Hugues Duncan, Pamela Whitfield,
Yvon Le Page and Yaser Abu-Lebdeh

**Energy, Mining and Environmental Portfolio
National Research Council of Canada**

High voltage material (5 V range)

- Higher energy and power densities
EV, HEV, PHEV
- Usually spinel compounds of the general formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (M = Ni, Co, Cu, Cr, Ti and Al)
- Requires electrolytes that are stable at high voltage



$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO)

- ✓ Red-ox potential of 4.7 V vs Li^+/Li
- ✓ Capacity of 148 mAh/g
- ✓ No Cobalt
- ✓ Commercially available

Nanomyte® SP-10 and Nanomyte® SP-15 from NEI

- Capacity fade at high temperature and high rate
- Promotes electrolyte decomposition

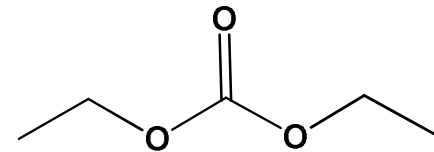
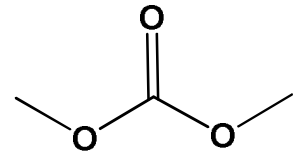
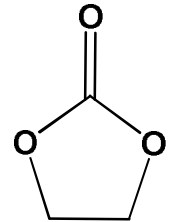
Conventional electrolytes and LNMO

LiPF_6 in a mixture of cyclic (EC) and linear (DMC, DEC) carbonate solvents

Undergoes oxidative decomposition at high voltage (4.5 V):

Poor CEI layer (poor long term cycling)

- Rapid capacity fade
- Rise in impedance



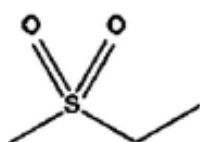
Potential alternatives to carbonates

- Ionic liquids: Salts that are liquid below 100 °C

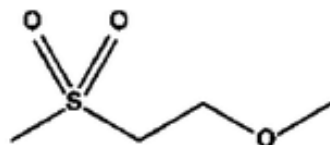
Usually a large cation and/or large anion

❖ N-, P- and S- based

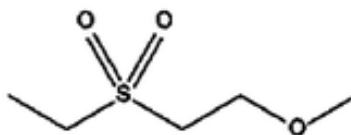
- Sulfones: -SO₂- group



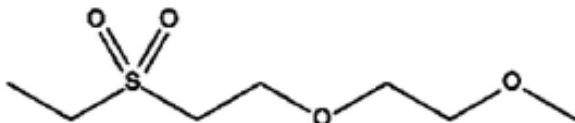
EMS



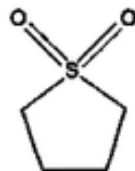
MEMS



EMES



EMEES



TMS



Dinitriles

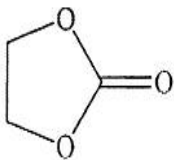
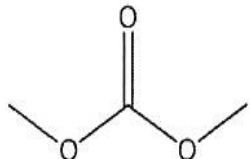
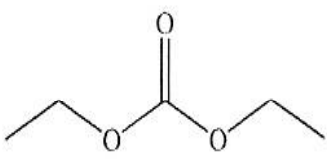
- Wide electrochemical window (7-8 V)
- Good solvating properties
- High boiling and flash point
- Commercially available and relatively cheap (ADN).
- Poor compatibility with graphite: needs co-solvent and additives



n

1	Malononitrile	MAN
2	Succinonitrile	SCN
3	Glutaronitrile	GLN
4	Adiponitrile	ADN
5	Pimelonitrile	PMN
6	Suberonitrile	SUN
7	Azelanitrile	AZN
8	Sebaconitrile	SEN

Table I. List of physical properties of dinitrile solvents and common carbonate solvents used in lithium electrolytes: ϵ is dielectric constant, η is viscosity, T_m is melting point, T_b is boiling point, T_f is flash temperature, T_{auto} is auto-ignition temperature.

	Structure	ϵ	$\eta(\text{cp})$	$T_m(^{\circ}\text{C})$	$T_b(^{\circ}\text{C})$	$T_f(^{\circ}\text{C})$	$T_{auto}(^{\circ}\text{C})$
EC		89	2 @ 40°C	35	244	150	465
DMC		3	0.7	3	90	18	458
DEC		3	0.8	-43	127	25	445
Acetonitrile*	CH ₃ CN	37	0.3	-48	81	2	523
Dinitriles	CN(CH ₂) _n CN						
	n						
Malononitrile (MAN*)	1	48 @ 30°C	solid	31	220	86	—
Succinonitrile (SCN*)	2	55 @ 55°C	2.7 @ 60°C	54	266	113	—
Glutaronitrile (GLN)	3	37	5.3	-29	287	113	—
Adiponitrile (ADN)	4	30	6.1	1	295	163	550
Pimelonitrile (PMN)	5	28	7.6	-31	175 @ 14 mmHg	112	455
Suberonitrile (SUN)	6	25	8.2	-4	325	110	—
Azelanitrile (AZN*)	7	23	8.7	-18	209 @ 33 mmHg	>110	—
Sebaconitrile (SEN)	8	22	10.7	8	200	>113	—

*Not used in this work but added for comparison

Salts and co-solvents

Salts:

- LiTFSI: soluble, corrode Al at high voltage
- LiPF₆: insoluble in dinitriles
- LiBF₄: slightly soluble in dinitrile , does not corrode Al
- LiBOB: sparingly soluble, used as co-salt, better SEI on graphite and CEI on LNMO

Co-solvents:

- EC: form good SEI and CEI layers
- DMC: improves conductivity

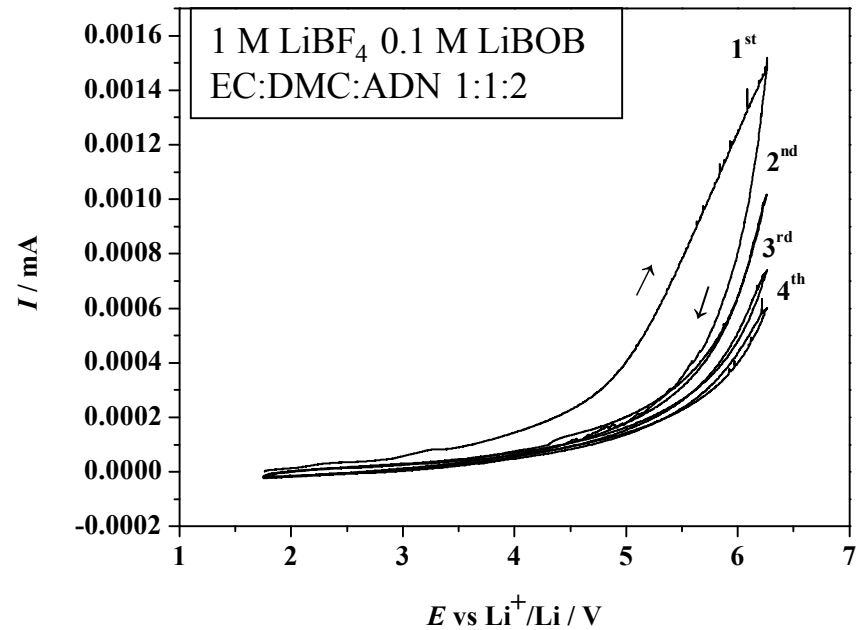
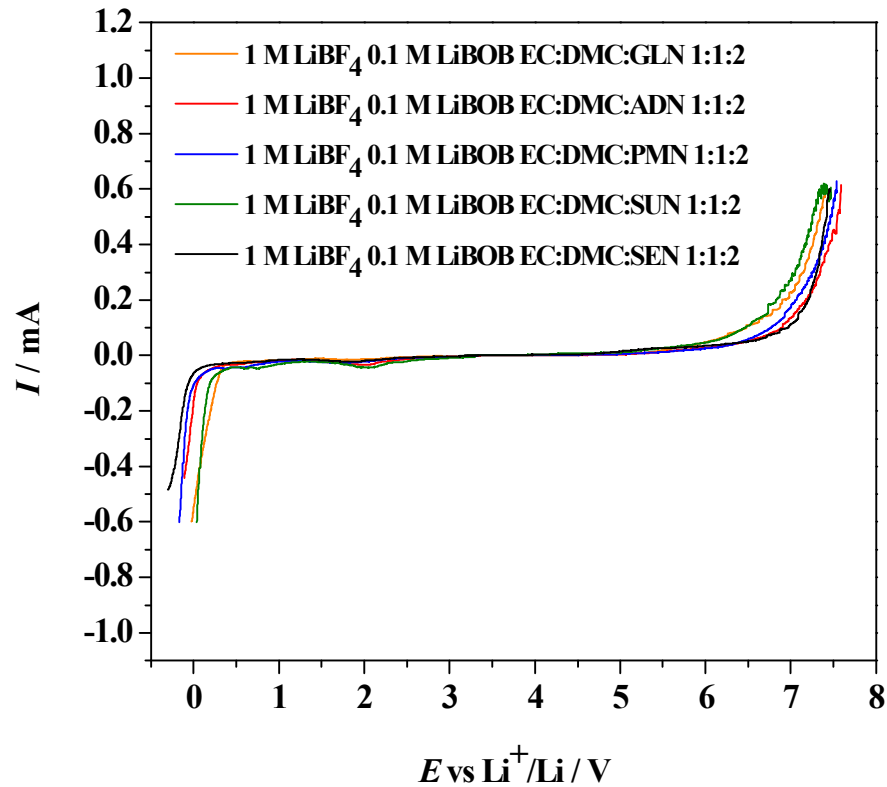
Electrolyte formulation

Binary: 1 M LiBF_4 0.1 M LiBOB EC:dinitrile 1:1

Ternary: 1 M LiBF_4 0.1 M LiBOB EC:DMC:dinitrile 1:1:2

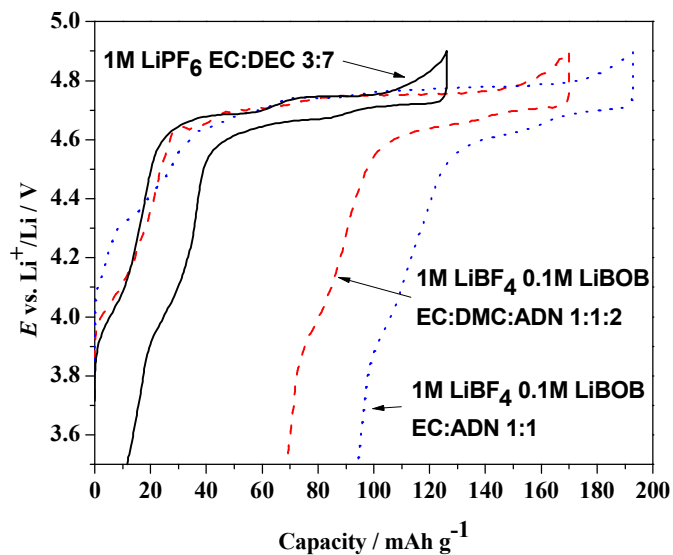
- Amatucci *et al.*: 1 M LiTFSI 0.25 M LiBF_4 ADN with FEC and VC additives, MCMB/Li and MCMB/ LiCoO_2
- Lex-Balducci *et al.*: 0.9 M LiBF_4 EC:ADN 1:1, graphite
- Abu-Lebdeh *et al.*: 1 M LiTFSI 0.1 M LiBOB EC:ADN 1:1, MCMB/ LiCoO_2
- Okada *et al.*: 1 M LiBF_4 0.1 M LiBOB EC:DMC:sebaconitrile 1:1:2, $\text{Li}_2\text{NiPO}_4\text{F}$ (few cycles)

Electrochemical window and Al-corrosion

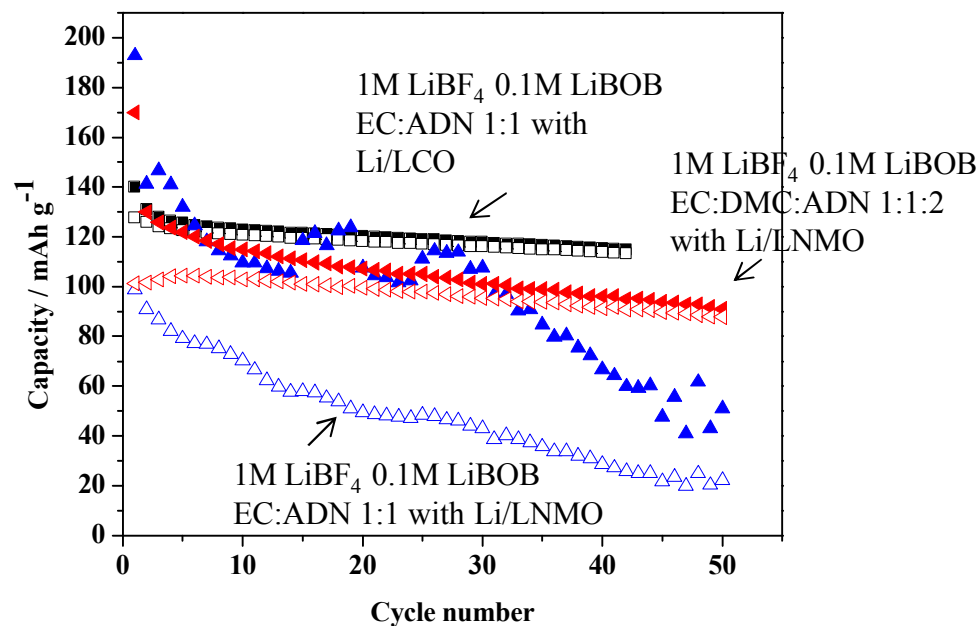
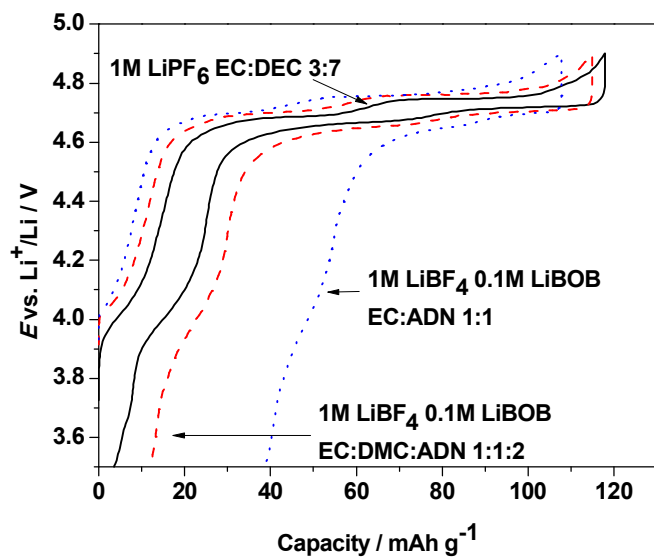


Battery performance

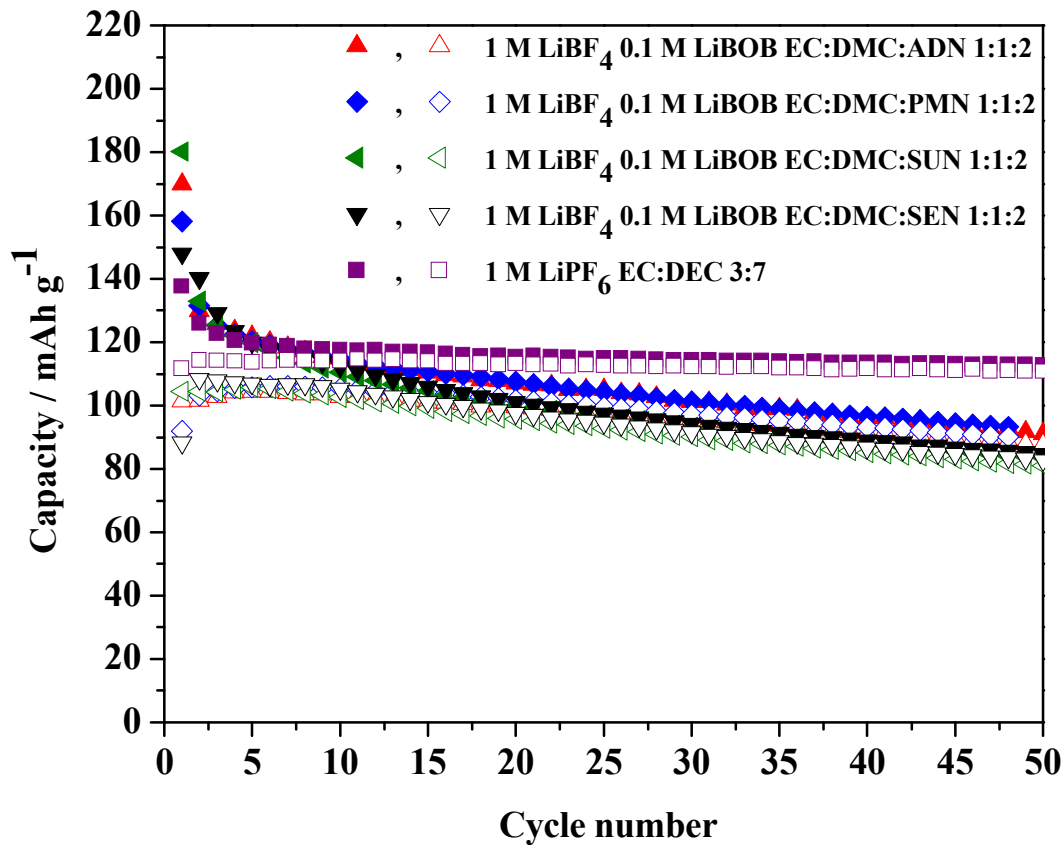
1st cycle



10th cycle

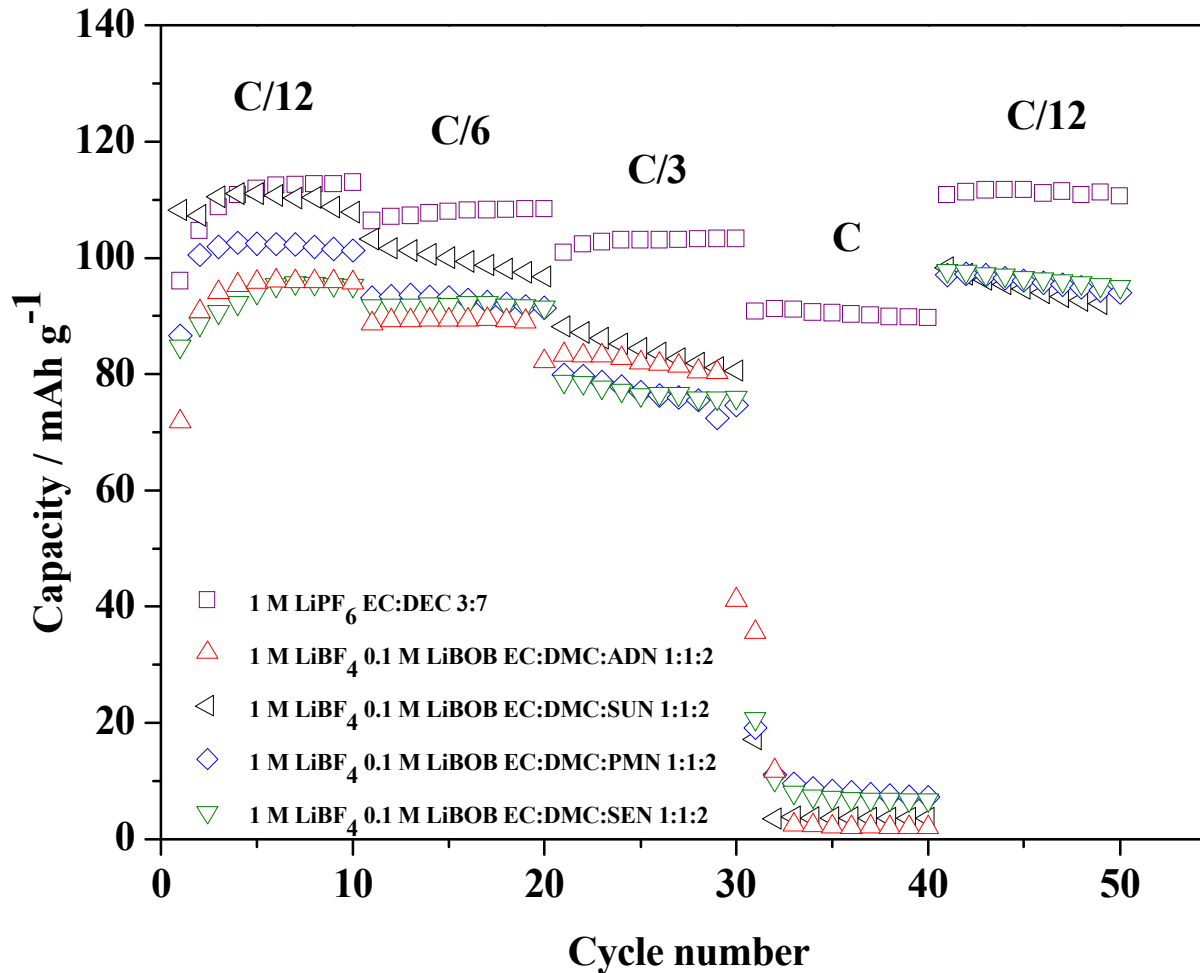


Battery performance



Shorter dinitriles (PMN and ADN) has higher capacities and lowest capacity fade (~ 13% over 50 cycles)

Battery performance

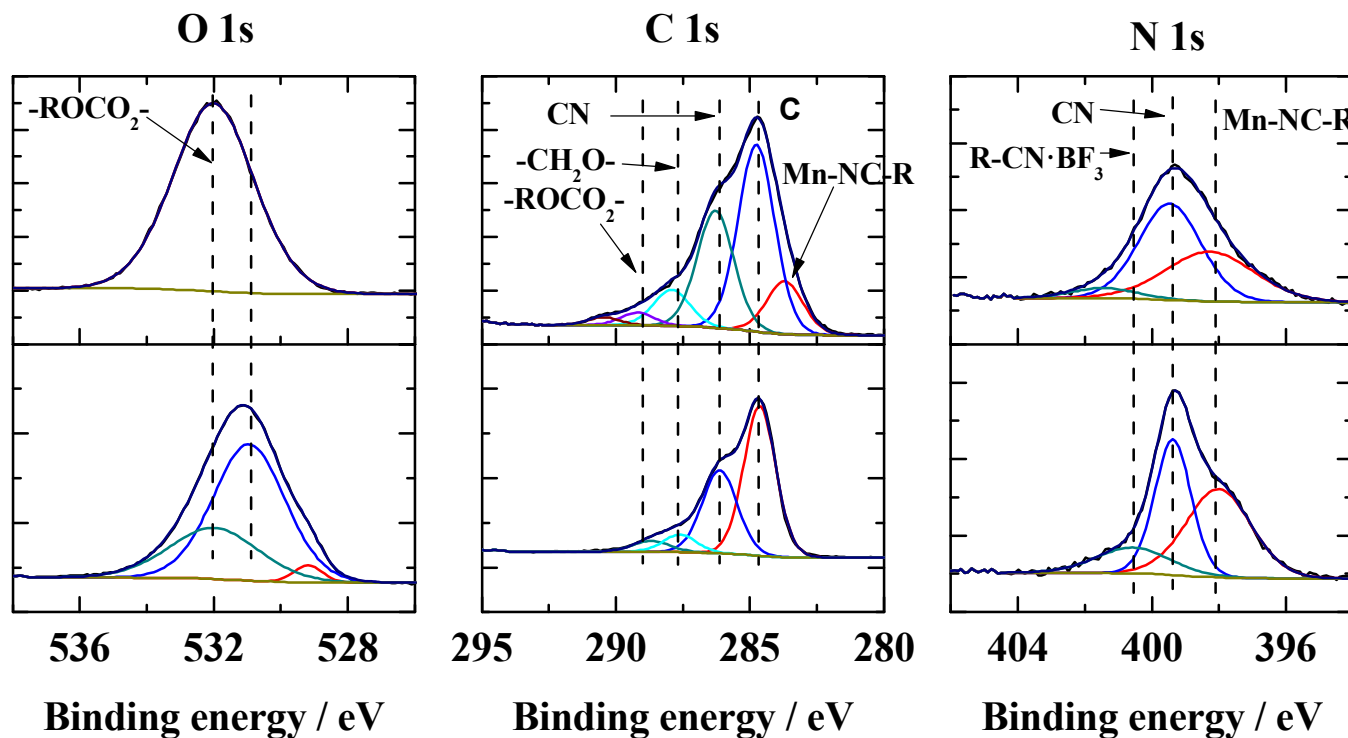


Dinitriles-based electrolytes has lower conductivities and possibly lower transport number (viscosity: ~ 8 cP, conductivities: 2-3.5 mS)

Attenuated total reflectance infrared spectra

	C≡N	C≡N	C=O	C=O	C-O	C-O
	in neat solvents	in LiBF ₄ electrolyte	in neat solvents	in LiBF ₄ electrolyte	in neat solvents	in LiBF ₄ electrolyte
EC			1795	1795	1389	1391
			1770	1762	1155	1405
						1155
						1196
DMC			1749	1740	1260	1264
				1723		1329
ADN	2246	2246				
		2270				
EC:DMC:ADN	2246	2246	1800	1801	1389	1390
		2271	1774	1774	1157	1405
			1750	1750	1276	1160
				1723		1196
						1279
						1317

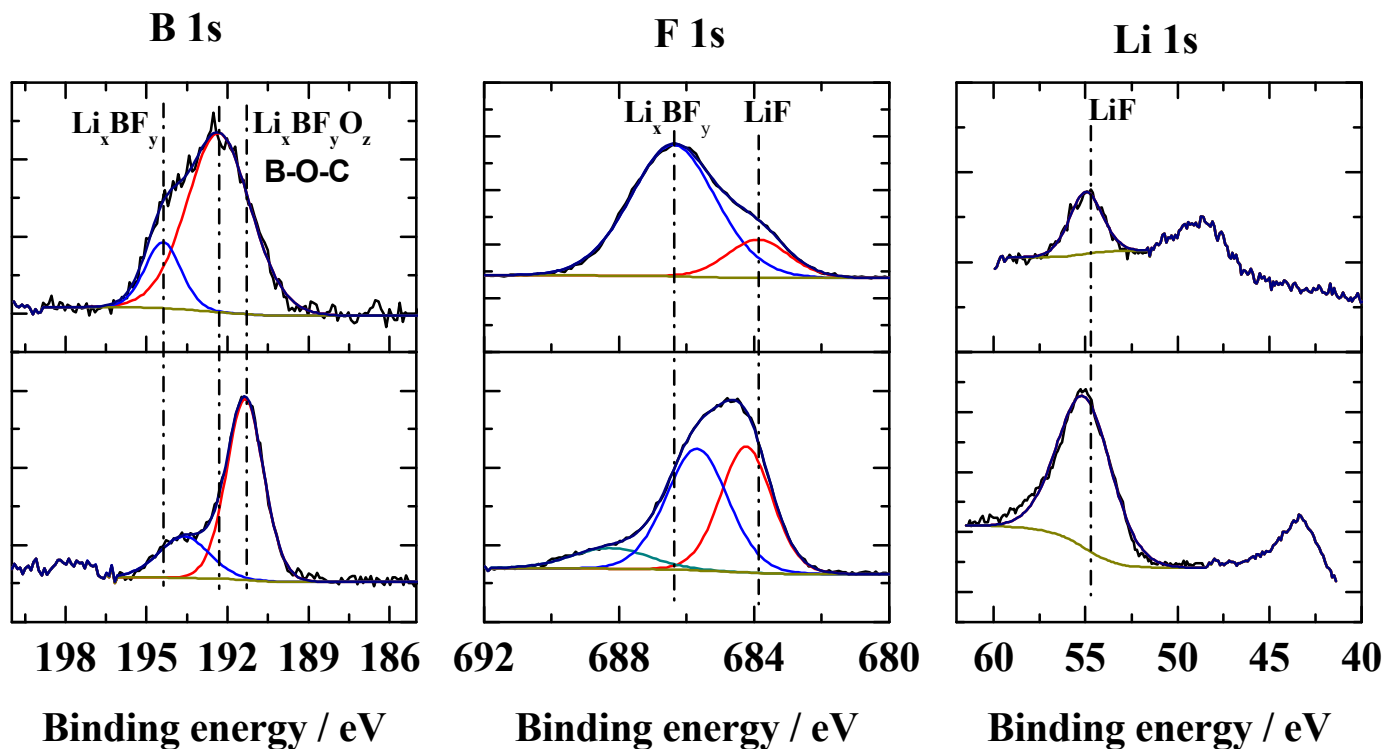
X-Ray Photoelectron Spectroscopy (XPS)



1M LiBF₄ 0.1M LiBOB
EC:DMC:ADN 1:1:2

1M LiBF₄ 0.1M LiBOB
EC:ADN 1:1

X-Ray Photoelectron Spectroscopy (XPS)



1M LiBF₄ 0.1M LiBOB
EC:DMC:ADN 1:1:2

1M LiBF₄ 0.1M LiBOB
EC:ADN 1:1

Conclusions

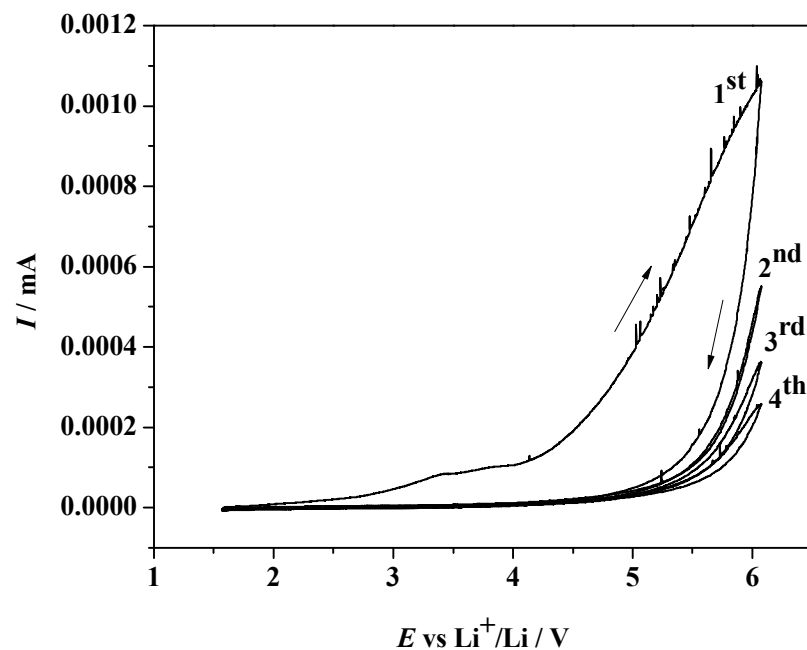
- Dinitriles in ternary electrolyte formulation with EC and DMC exhibits excellent electrochemical stability window (6 V).
- The ternary electrolyte performed fairly well with Li/LiNi_{0.5}Mn_{1.5}O₄ half cell, a 4.7 V system.
- There is a slight correlation between irreversible capacities and chain length with the shorter Adiponitrile and Pimelonitrile showing slightly better capacities and lower capacity fade.
- LiBOB and DMC plays important roles in CEI stabilization and in the protection of LiBF₄ from oxidative decomposition.
- Dinitriles compete with carbonates in solvating Li ions and participate in reactions at the interface as shown in IR and XPS.



Questions

Aluminum corrosion

1 M LiBF₄ EC:ADN 1:1



Crystalline structure

