Dinitrile-based electrolytes for high voltage lithium-ion batteries

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Dinitrile-based Electrolytes for high voltage Lithium-Ion Batteries

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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

  $LiM_xMn_{2-x}O_4$ (M = Ni, Co, Cu, Cr, Ti and Al)

- Requires electrolytes that are stable at high voltage

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)

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

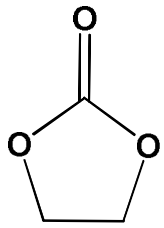
Nanomyte® SP-10 and *Nanomyte® SP-15* from NEI

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

Conventional electrolytes and LNMO

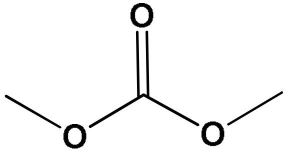
$LiPF_6$ in a mixture of cyclic (EC) and linear (DMC, DEC) carbonate solvents

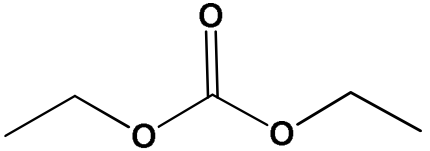
Undergoes oxidative decomposition at high voltage (4.5 V):



Poor CEI layer (poor long term cycling)

- ➢ Rapid capacity fade
- ➢ Rise in impedance





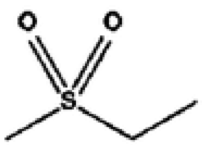
Potential alternatives to carbonates

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

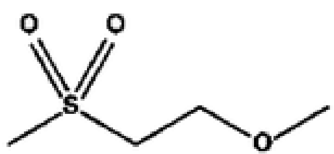
  Usually a large cation and/or large anion

  ❖ N-, P- and S- based

- Sulfones: -SO_2- group



EMS



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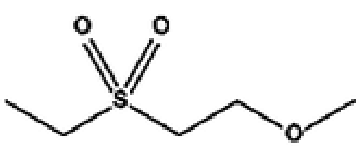
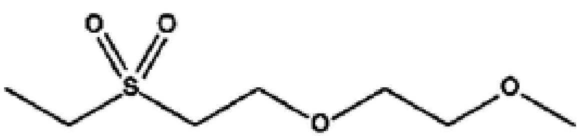


EMES



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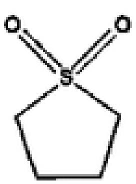


TMS

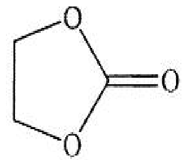
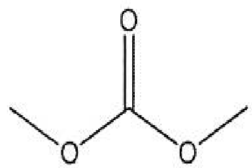
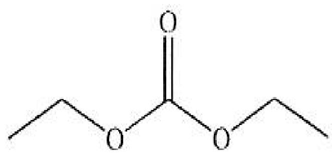
Dinitriles

- 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

$$N\equiv C-(CH_2)n-C\equiv N$$

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	η(cp)	T_m(°C)	T_b(°C)	T_f(°C)	T_{auto}(°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_3CN	37	0.3	−48	81	2	523
Dinitriles	$CN(CH_2)_nCN$						
	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
- $LiPF_6$: insoluble in dinitriles
- $LiBF_4$: 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

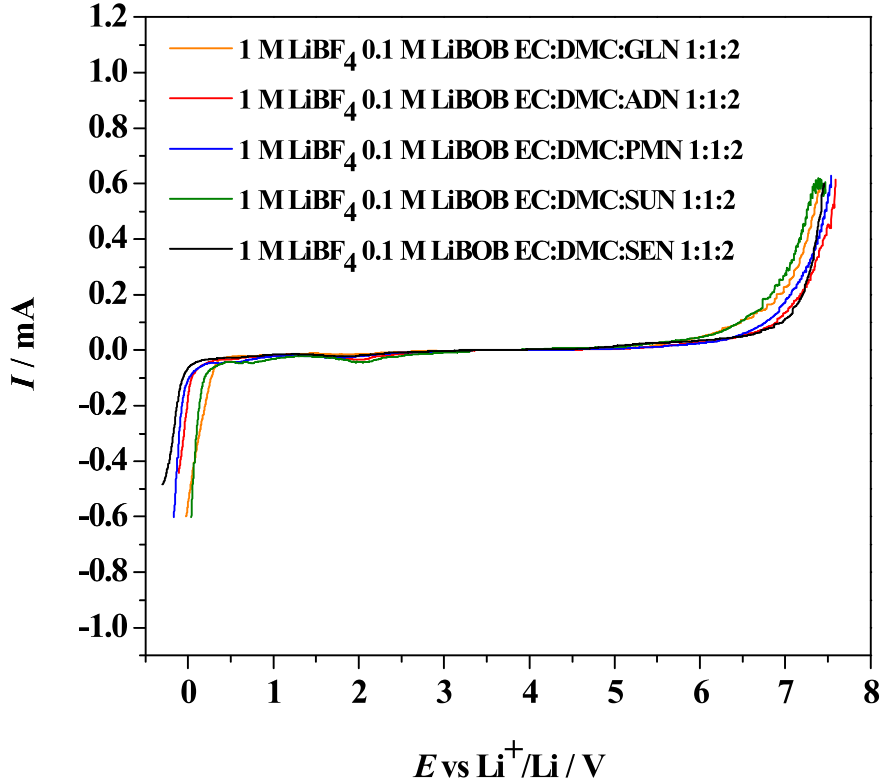
- Amatucci *et al.*: 1 M LiTFSI 0.25 M $LiBF_4$ ADN with FEC and VC additives, MCMB/Li and MCMB/$LiCoO_2$

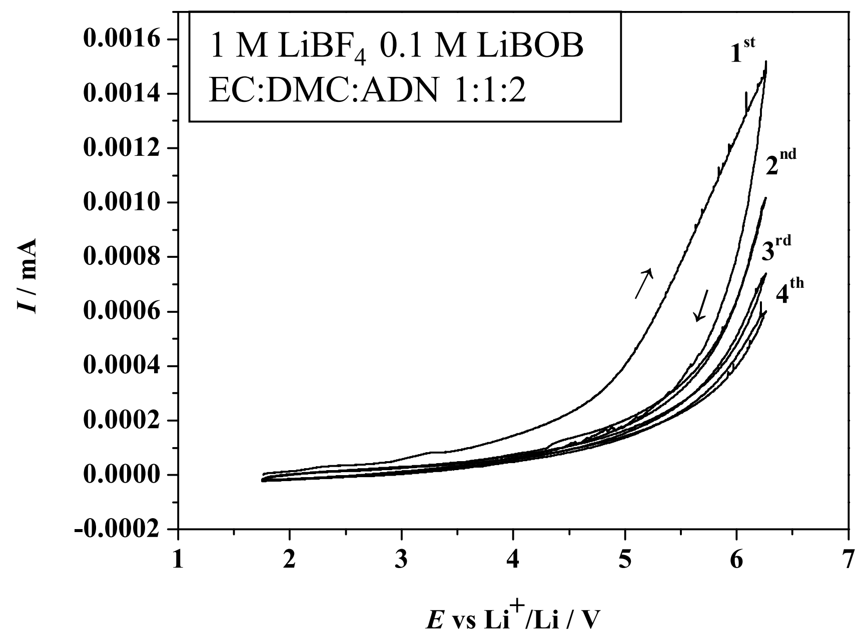
- Lex-Balducci *et al.*: 0.9 M $LiBF_4$ EC:ADN 1:1, graphite

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, Li_2NiPO_4F (few cycles)

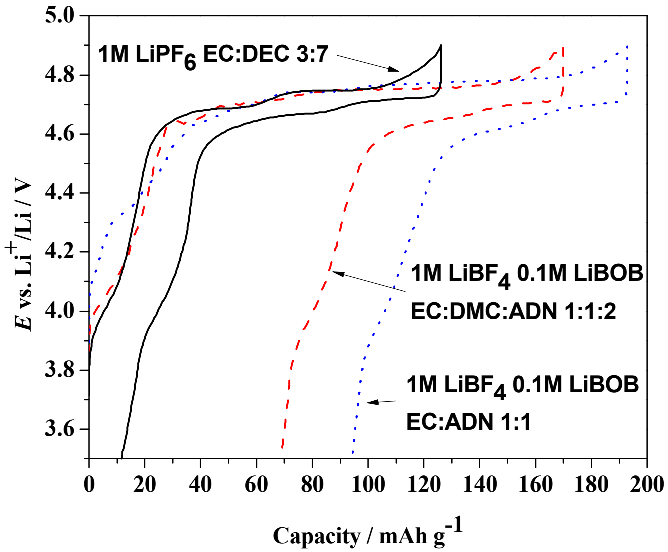
Electrochemical window and Al-corrosion



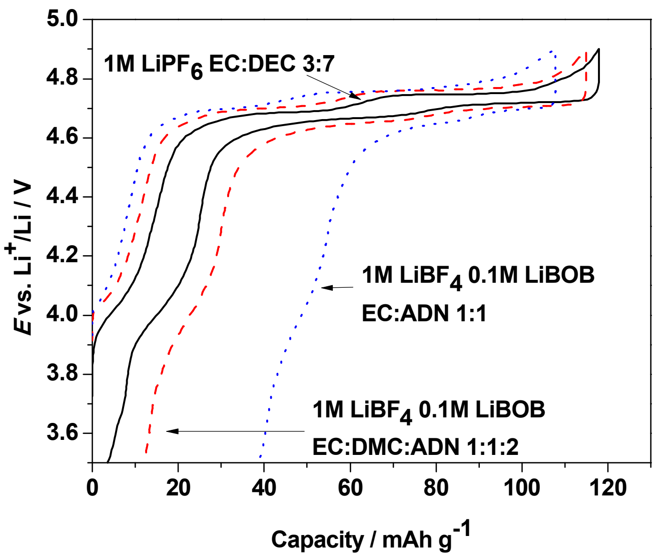


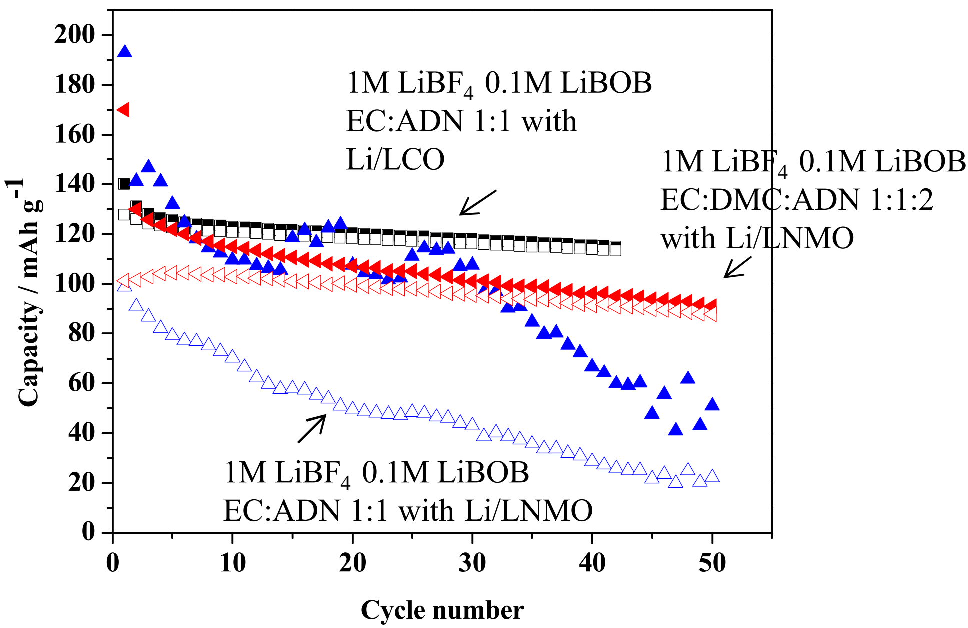
Battery performance

1st cycle

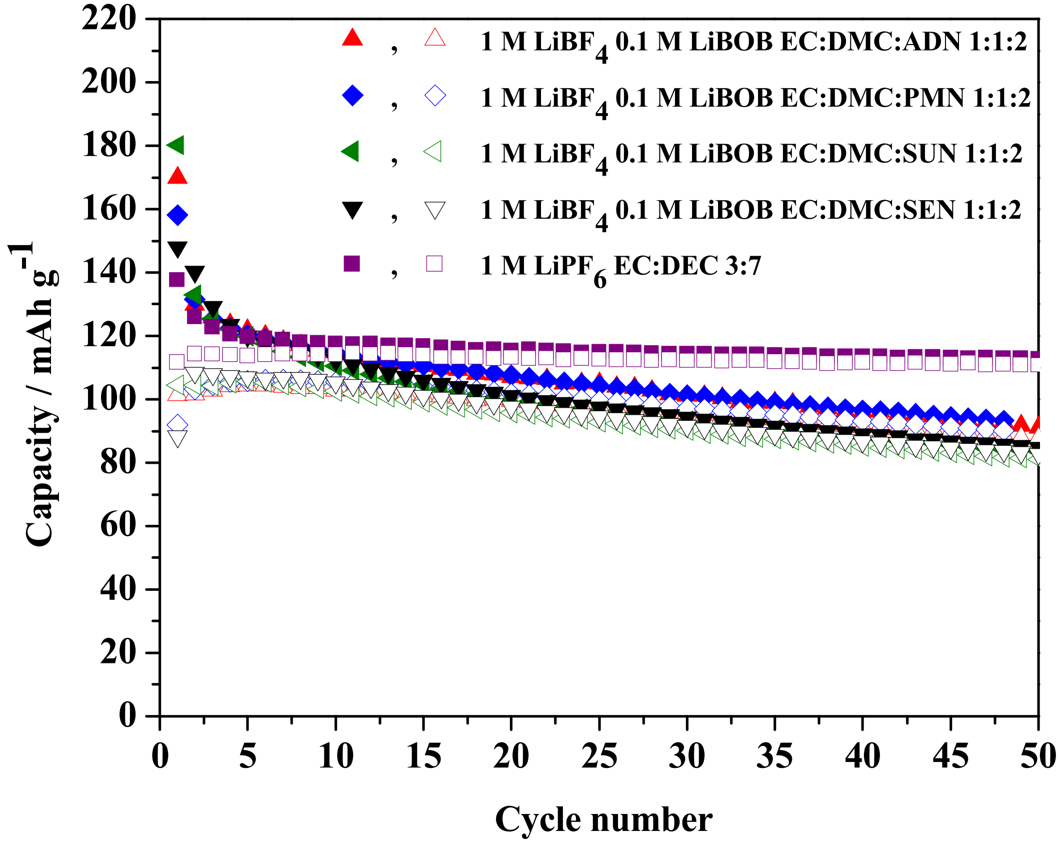


10th cycle



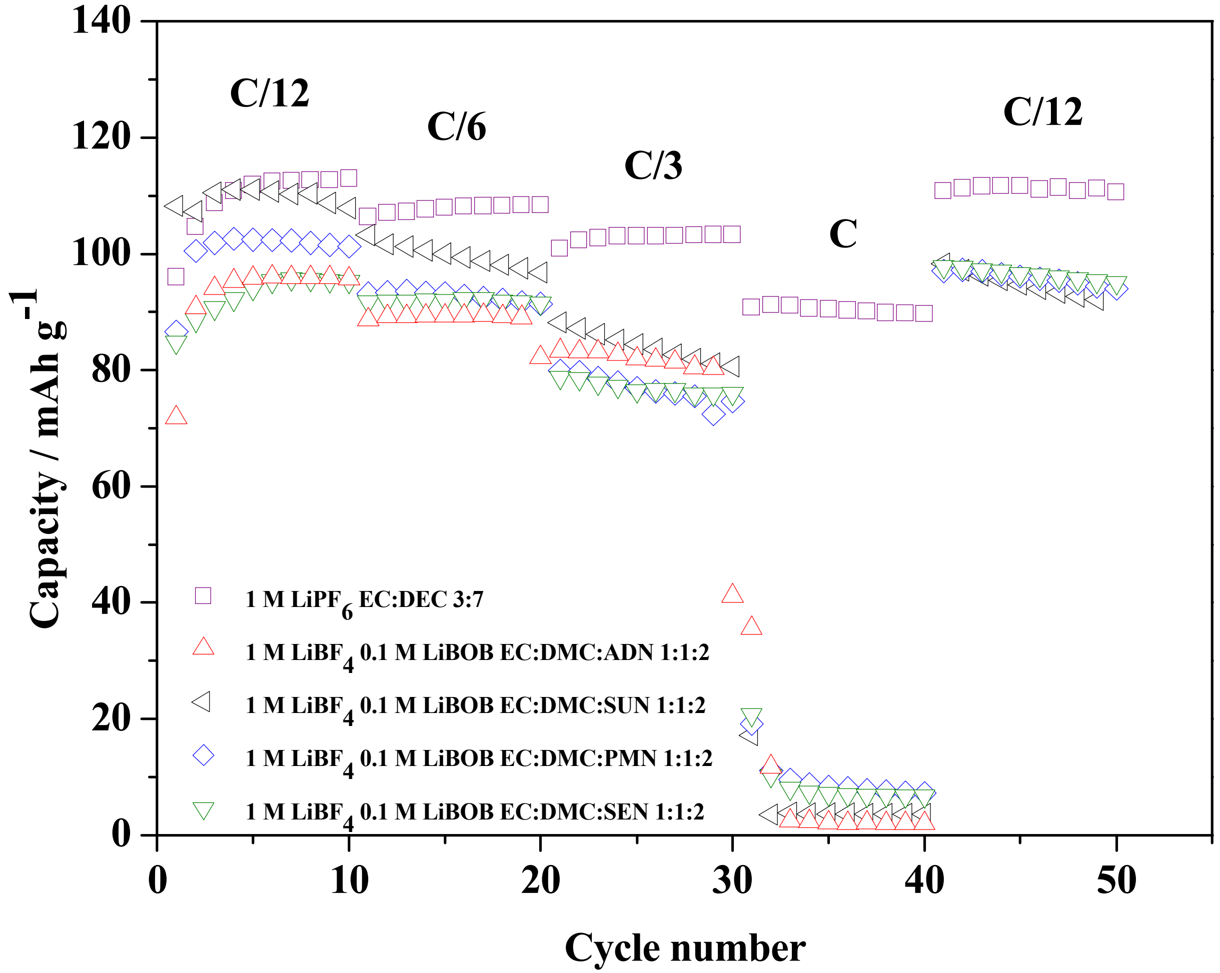


Battery performance



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

Battery performance

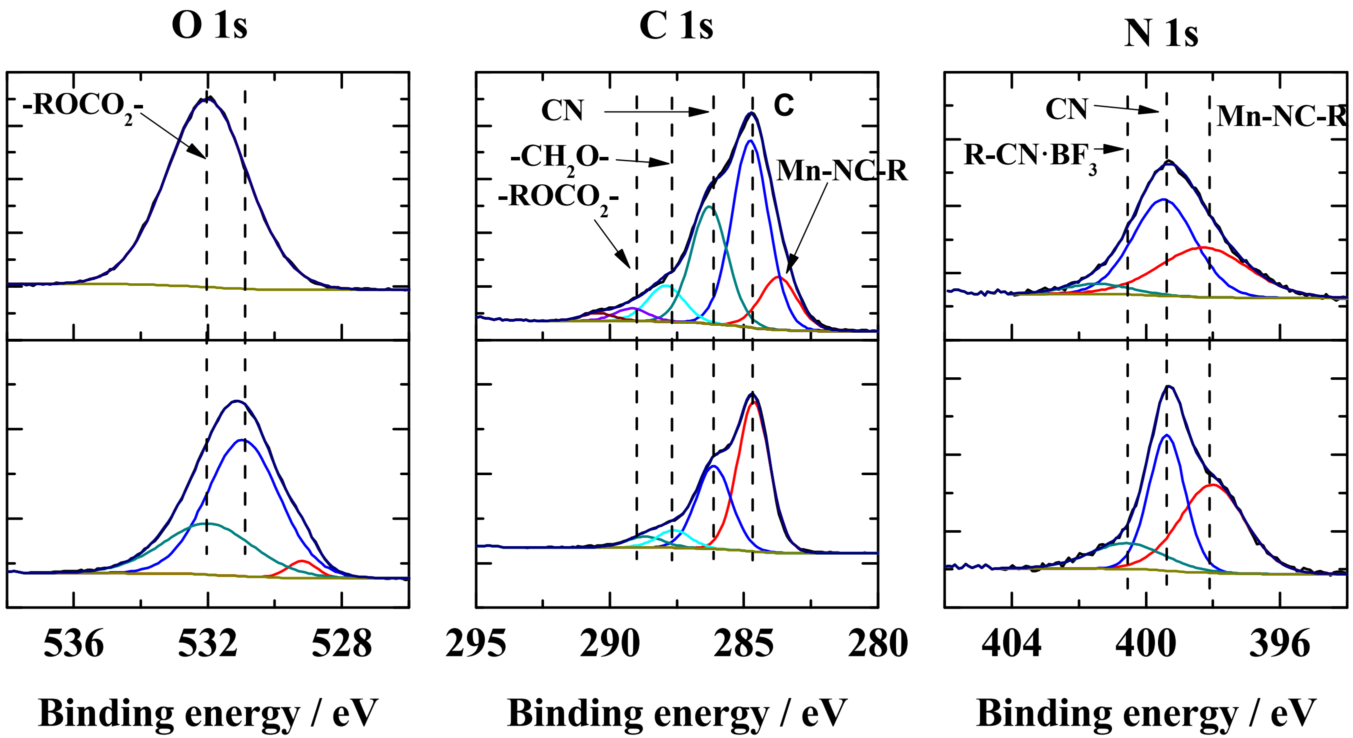


Dinitriles-based electrolytes has lower conductivities and possibly lower transport number (viscosity: ~ 8 cP, conductivities: 2-3.5 mS)

Attenuated total reflectance infrared spectra

	C≡N in neat solvents	C≡N in $LiBF_4$ electrolyte	C=O in neat solvents	C=O in $LiBF_4$ electrolyte	C-O in neat solvents	C-O 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

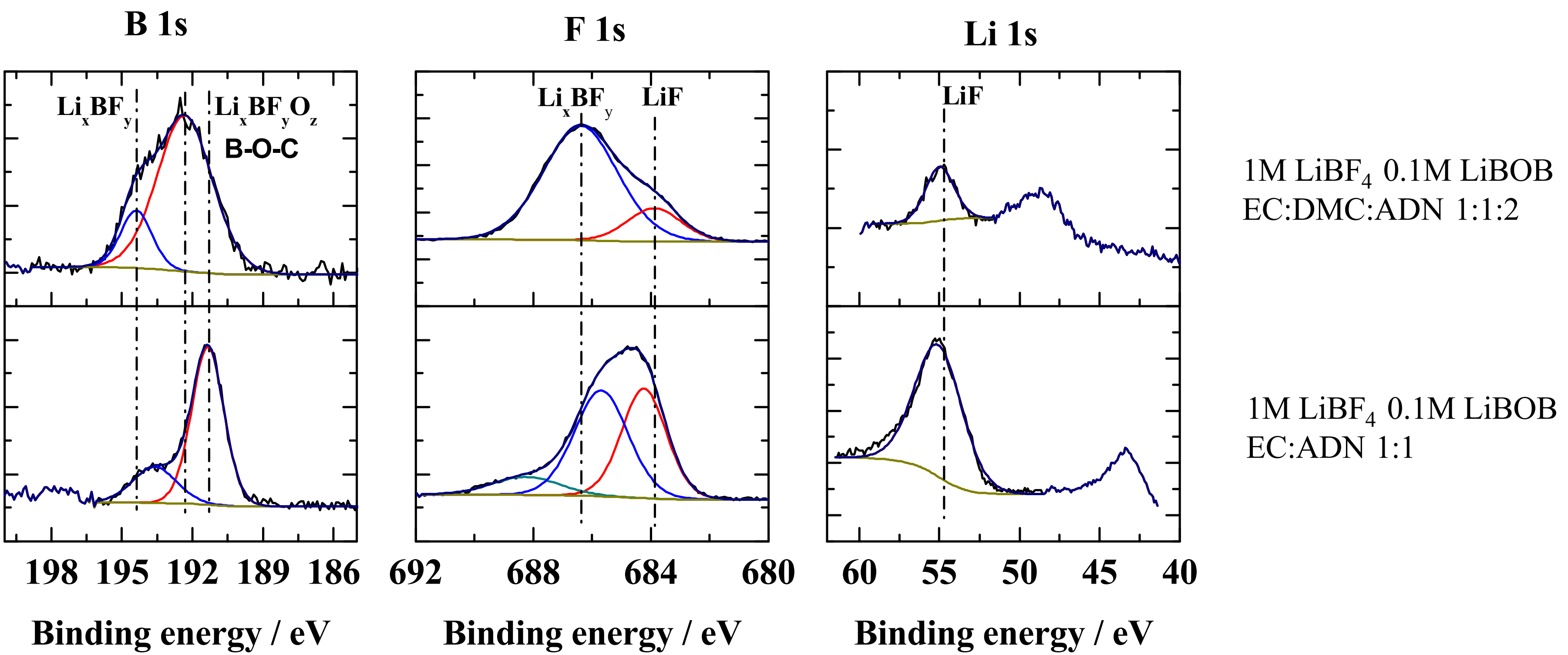
X-Ray Photoelectron Spectroscopy (XPS)



1M $LiBF_4$ 0.1M LiBOB
EC:DMC:ADN 1:1:2

1M $LiBF_4$ 0.1M LiBOB
EC:ADN 1:1

X-Ray Photoelectron Spectroscopy (XPS)



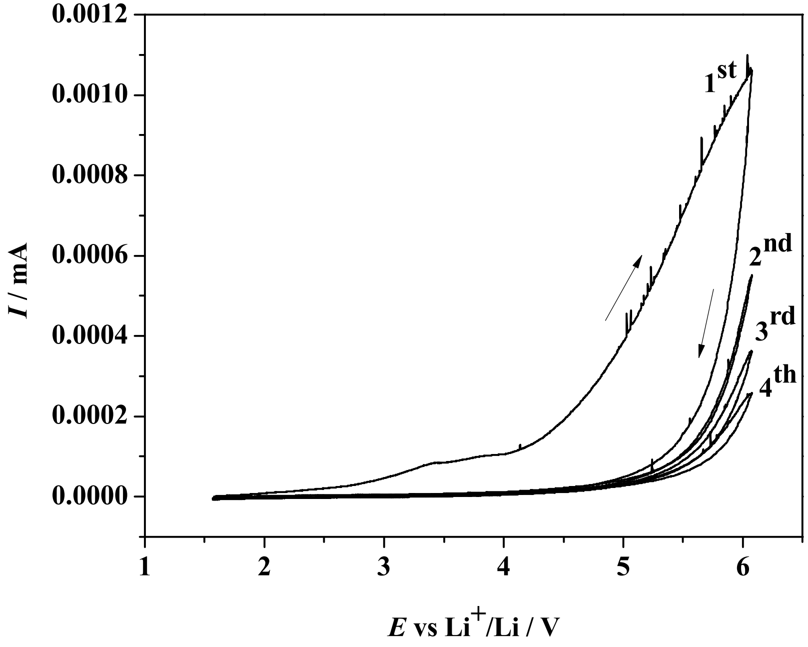
Conclusions

- Dinitriles in ternary electrolyte formulation with EC and DMC exhibits excellent electrochemical stability window (6 V).
- The ternary electrolyte performed fairly well with Li/$LiNi_{0.5}Mn_{1.5}O_4$ 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 $LiBF_4$ from oxidative decomposition.
- Dinitriles compete with carbonates in solvating Li ions and participate in reactions at the interface as shown in IR and XPS.

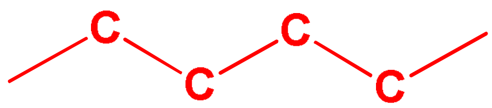
Questions

Aluminum corrosion

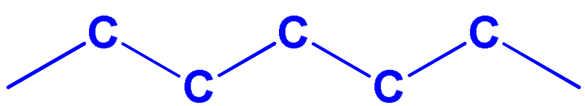
1 M $LiBF_4$ EC:ADN 1:1



Crystalline structure



Trans



Cis