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Electrolyte transport and stability

24-634 / 27-700: Energy Storage Materials and Systems

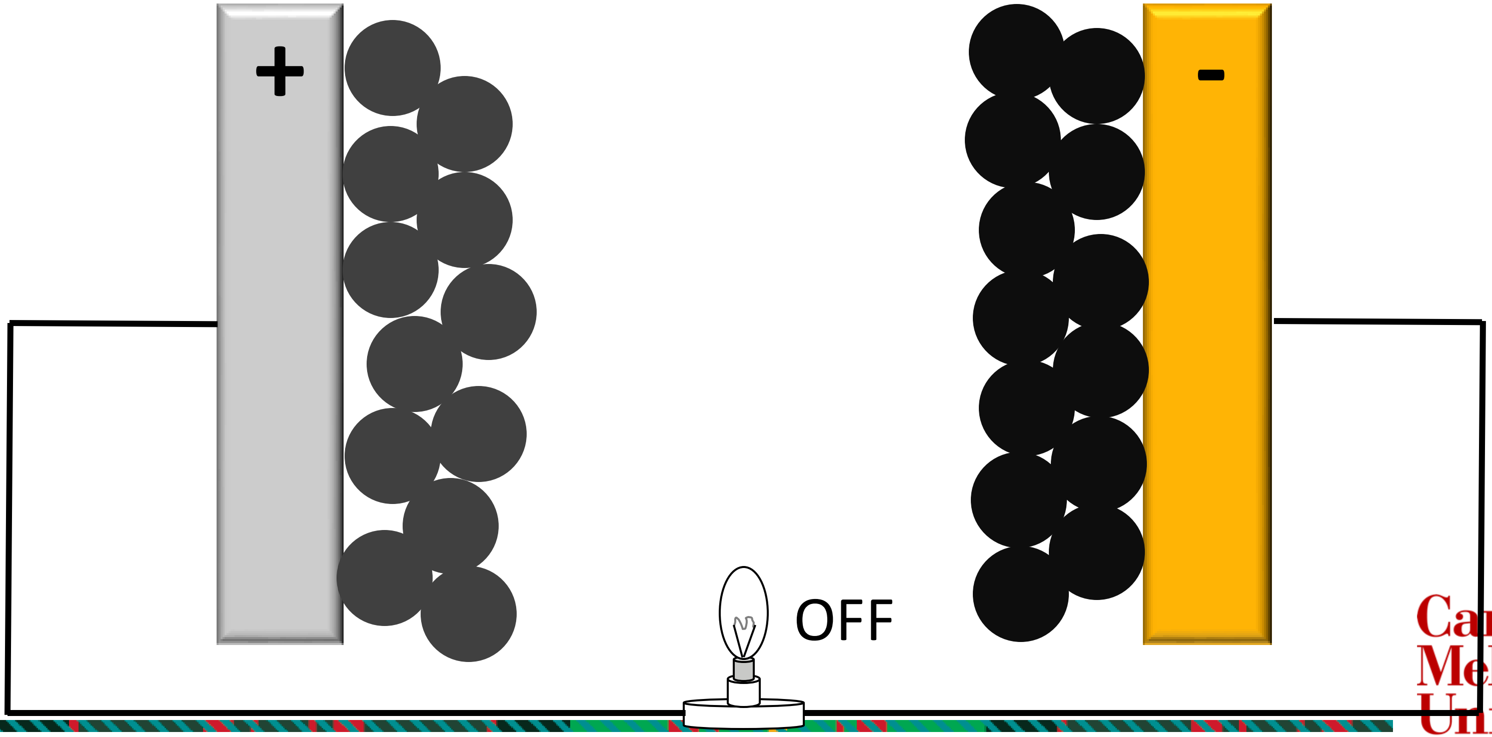
Roby Gauthier

Learning objectives

- Understand why the electrolyte is an important part of a cell.
- Understand the underlying physical principles and assumptions of the Nernst-Einstein and Stokes-Einstein transport equations.
- Compare different solvents, salts, additives, and electrolytes to see how they influence cell performance, degradation, and safety.
- Implement what you learned to select an appropriate electrolyte for a specific need.

Why is an electrolyte needed in a cell?

The positive and negative electrodes can't function properly if they are separated by vacuum, since lithium-ions need to be able to diffuse from one electrode to the other.



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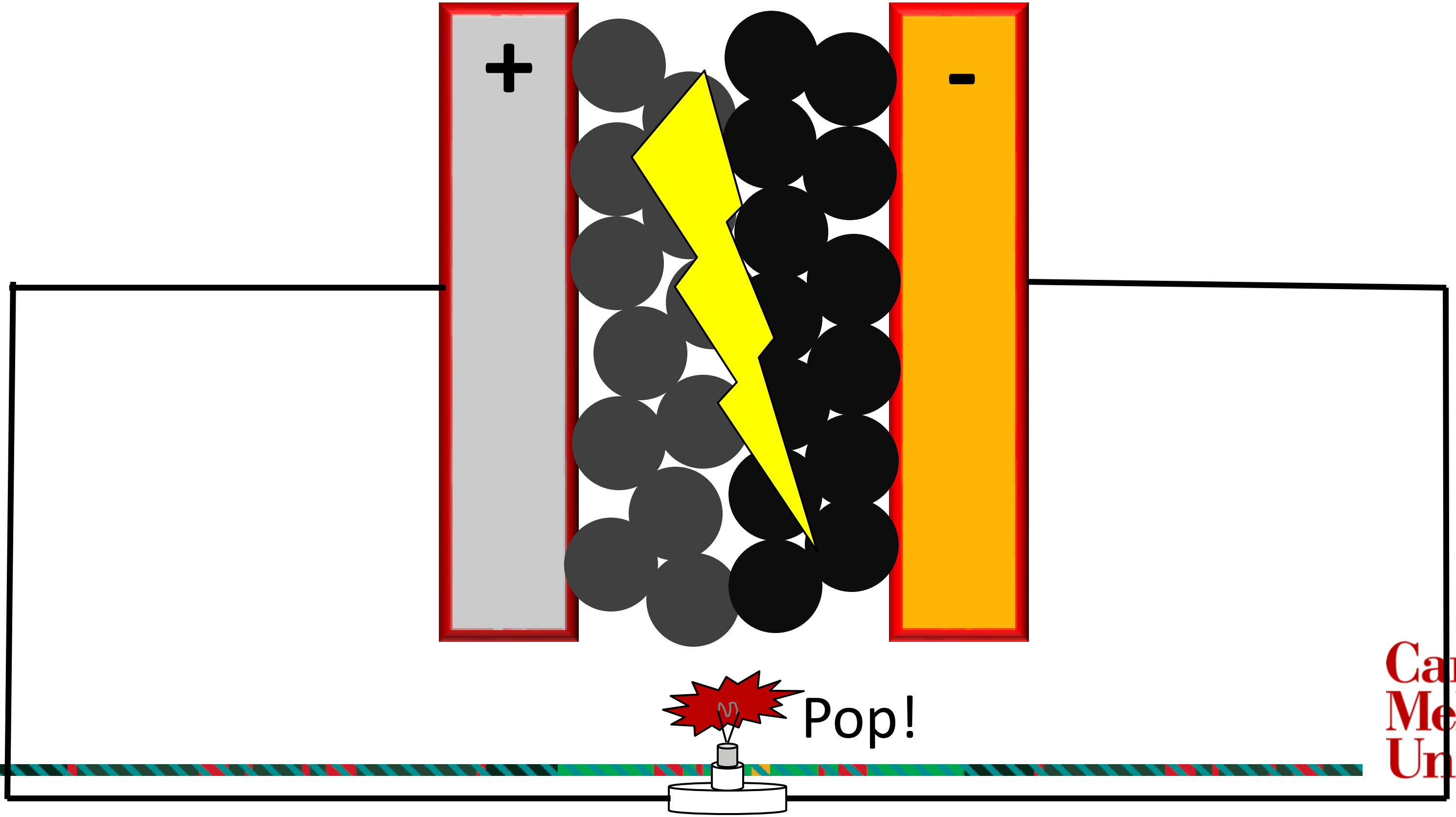
Why is an electrolyte needed in a cell?

If the electrodes are directly touching when charged, Li-ions can now diffuse, but the cell is in **short-circuit**. This cause rapid loss of energy and overheating.



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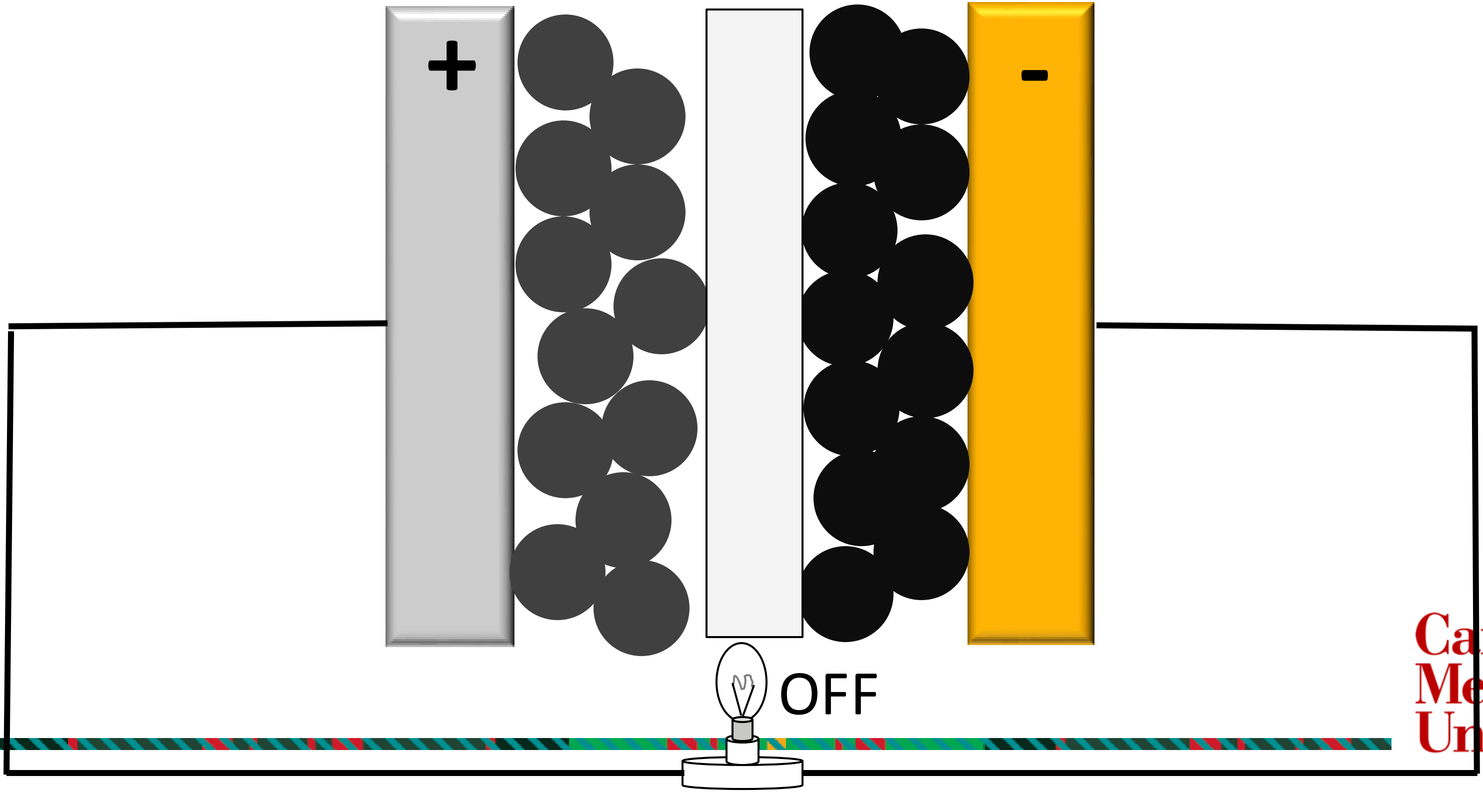
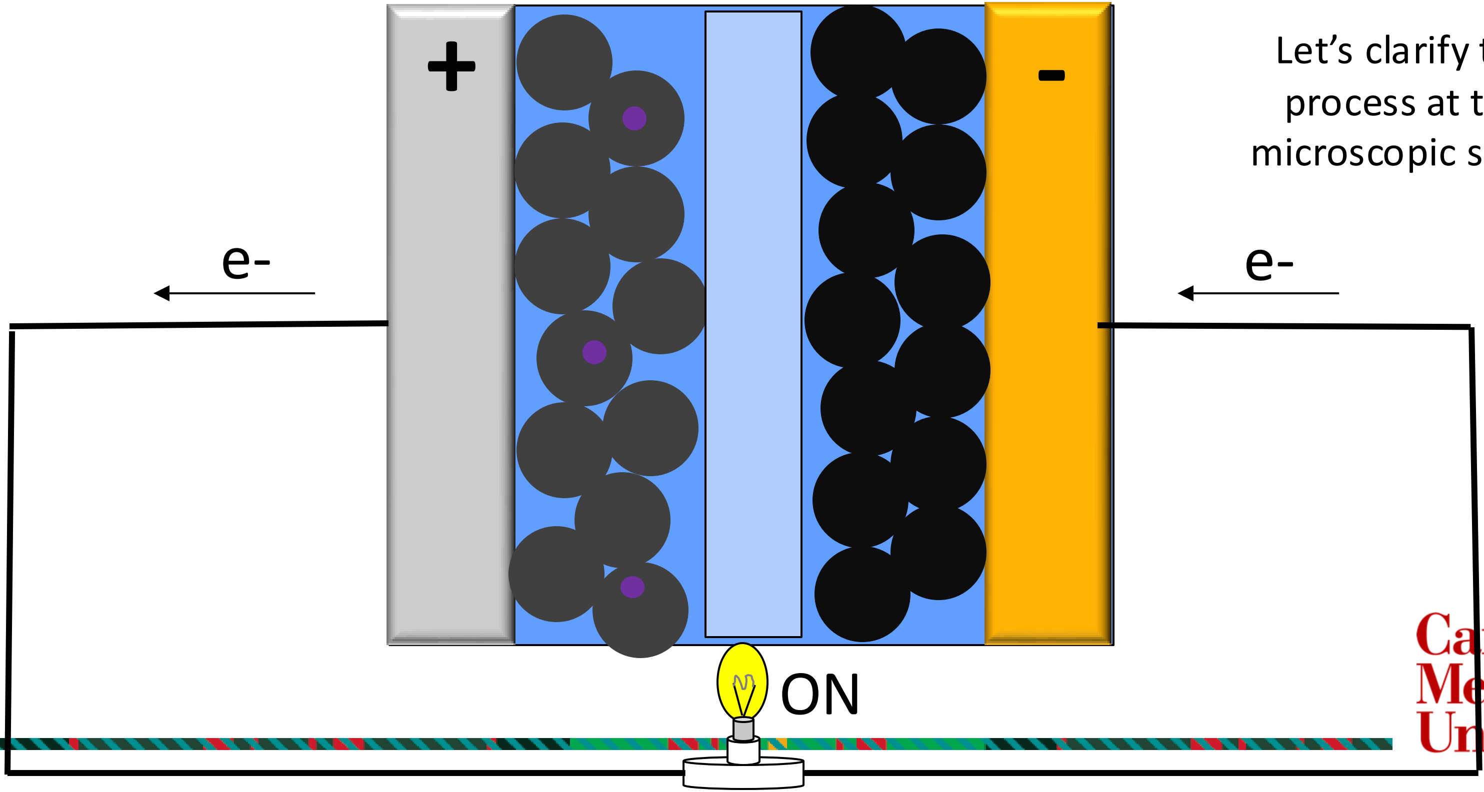
Why is an electrolyte needed in a cell?

To prevent this, we can separate the electrodes using a plastic separator. However, lithium ion still struggle to diffuse effectively.



Why is an electrolyte needed in a cell?

Adding the liquid electrolyte allow effective diffusion of the lithium-ion, completing the circuit.



Let’s clarify the process at the microscopic scale.

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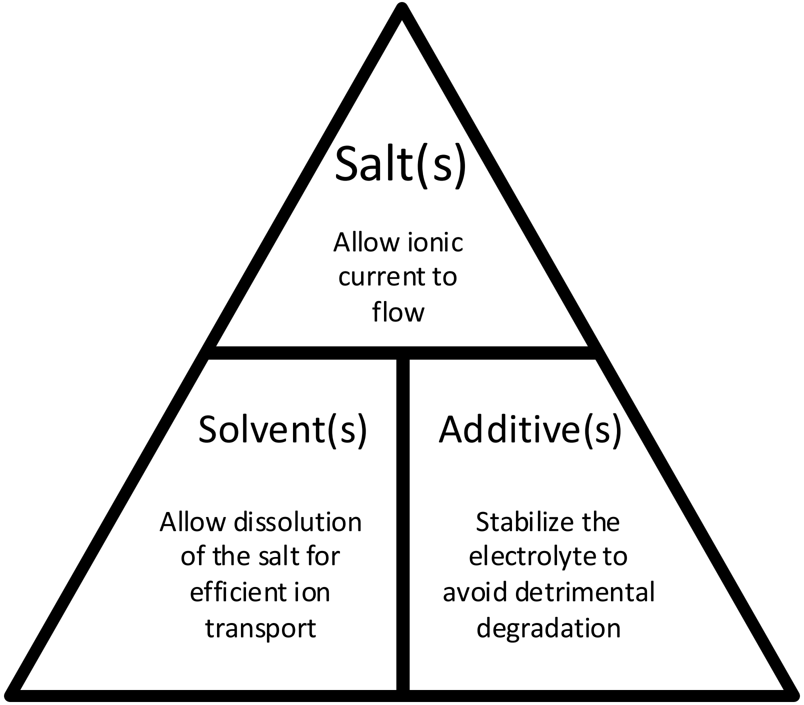
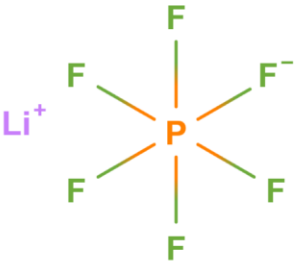
Three main components of a liquid electrolyte

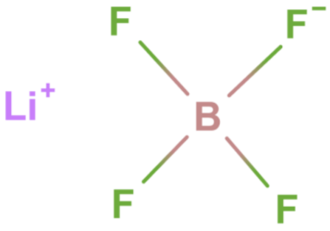


Salts

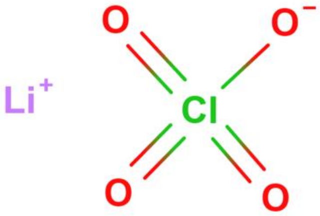
$LiPF_6$



$LiBF_4$

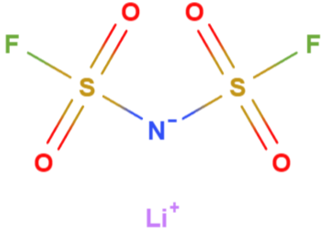


$LiClO_4$

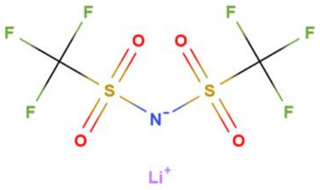


	Thermal stability	Conductivity	Electrochemical oxidation stability
	Decomposition temperature (°C)	Conductivity in EC/EMC 3:7 at 1M (25°C) (mS/cm)	Oxidation state of the central atom
$LiPF_6$	~80 [1]	9.33 [4]	+5
$LiBF_4$	>100 [1]	3.72 [4]	+3
$LiClO_4$	>100 [1]	6.26 [4]	+7
LiFSI	~140 [2]	9.73 [4]	-3
LiTFSI	~140 [3]	7.57 [4]	-3
NaOH	N/A	206 (5% wt.) [5]	-2
H_2SO4	N/A	211 (5% wt.) [5]	+6

LiFSI



LiTFSI



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[1] Chem. Rev. 2004, 104, 4303−4417 [2] RSC Adv., 2016, 6, 23327 [3] *Polymers* **2021**, *13*(5), 707 [4] Journal of Power Sources 196 (2011) 3623–3632 [5] CRC Handbook of Chemistry and Physics 95th editions

Solvent

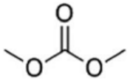
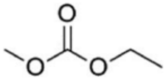
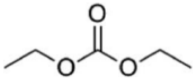
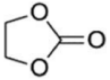
What solvent properties matter for a cell electrolyte?

Melting point

Influence low temperature performance

Viscosity η	**Permittivity ε_r**
Influence ion transport (Low viscosity is good)	Influence salt dissolution and ion transport (High permittivity is good)
Redox potentials Influence electrolyte stability (Large redox window is good, but oxidation at the cathode is still not well understood)	**Flash point** Influence flammability and safety (High flash point is good)

Solvents

Category	Compound	Abb.	Structure	η cP	Ref.	ε	Ref.	E^0_{red} *V vs Li/Li*$^+$	E^0_{ox} *V vs Li/Li*$^+$	Flash Point[b] °*C*
Linear carbonate	Dimethyl carbonate	DMC		0.59	68,69	3.08	70	0.10	7.06	16
						3.12	71,72			
	Ethyl methyl carbonate	EMC		0.65	73	2.4	74	0.10	6.97	23
						2.9	72			
						3.5	37			
	Diethyl carbonate	DEC		0.75	40,41,45	2.82	70–72	0.07	6.95	25
Cyclic carbonate	Ethylene carbonate	EC		1.9[c]	75	88.6[c]	76	0.27	7.19	143
						89.1	77			
						89.6	72			
						89.8	70,73			
						90.5	78			

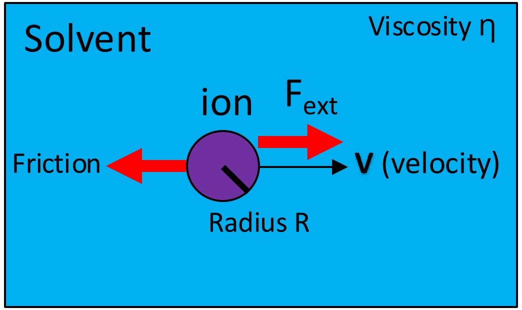
David S. Hall et al 2018 J. Electrochem. Soc. 165 A2365

Ion transport in electrolytes: self-diffusion

Stokes' law

(Derived from Navier-Stokes equation. Assumes laminar flow)

$$\vec{F}_{fric} = -6\pi R\eta\vec{v}$$



Definition of the mobility

$$\vec{v} = \mu\vec{F}_{ext}$$

R: ion radius
η: viscosity
μ: mobility
D: Diffusion constant
k_B : Boltzmann constant
T: Temperature
$\vec{v}$: ion velocity
$\overrightarrow{F_{fric}}$: Friction force
$\overrightarrow{F_{ext}}$: Exterior/applied force

Einstein relation

(Derived from the equipartition and fluctuation-dissipation theorems)

$$D = \mu k_B T$$

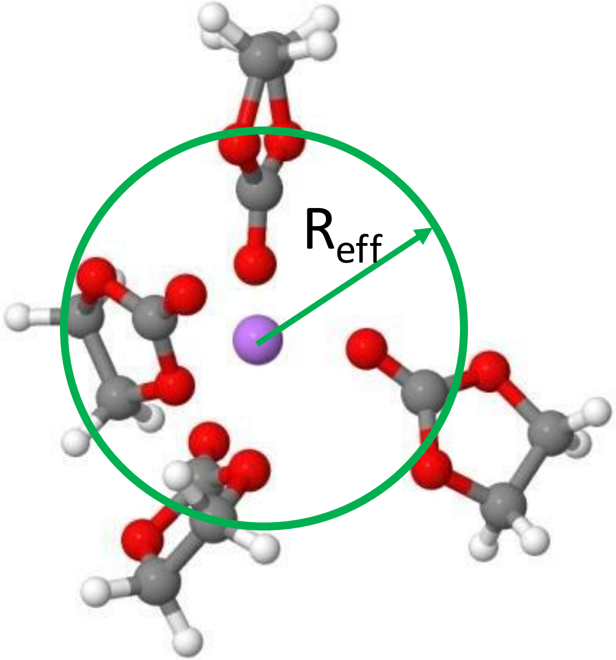
Using the definition of the mobility μ, we get:

$$D = \frac{k_B T}{6\pi\eta R}$$

How does this relate to charging speed?

What about the impact of solvation shells?

Quick overview of solvation shells: effective radius



$$D = \frac{k_B T}{6\pi\eta R_{eff}}$$

R_{eff}: Effective ion radius when considering the solvation shell

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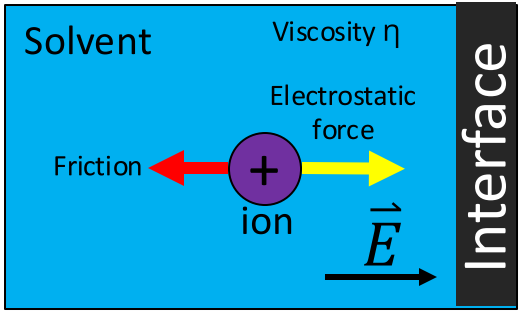
The Journal of Physical Chemistry C **2015** *119* (9), 4502-4515

Ion transport in electrolytes: ion conductivity at the interfaces



q_+: *charge of a positive ion*
n_+: *positive ions per unit of volume*
$< \vec{v_+} >$: Average velocity of positive ions
$\vec{E}$: Electric field
$\vec{J_+}$: Current due to the positive ions
σ_+: Conductivity due to the positive ions

Forces balance:

$$q_+ \vec{E} = 6\pi\eta R_{eff,+} < \vec{v}_+ >$$

Definition of the current density :

$$\vec{J}_+ = \sigma_+ \vec{E} = n_+ q_+ < \vec{v}_+ >$$

Conductivity:

$$\sigma_+ = \frac{n_+ q_+^2}{6\pi\eta R_{eff,+}}$$

Positive ion contribution

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Ion conductivity: contribution from positive and negative ions

$$\sigma = \frac{1}{k_B T}(n_+ q_+^2 D_+ + n_- q_-^2 D_-)$$

Nernst-Einstein equation

$$\Lambda = \frac{\sigma}{c} = \frac{F^2}{RT}(w_+ z_+^2 D_+ + w_- z_-^2 D_-)$$

Molar conductivity

q_- : charge of a negative ion

n_-: negative ions per unit of volume

D_+ or D_- :Diffusion constant of positive or negative ions

σ: Total conductivity from all ions

Λ: Molar conductivity

c: Molar concentration of salt

w_+ or w_- : Number of positive or negative ions in the salt (For calcium chloride, $w_+ = 1$ and $w_- = 2$)

z_+ or z_- : Charge number of the positive or negative ions (For calcium chloride, $z_+ = 2$ and $z_- = 1$)

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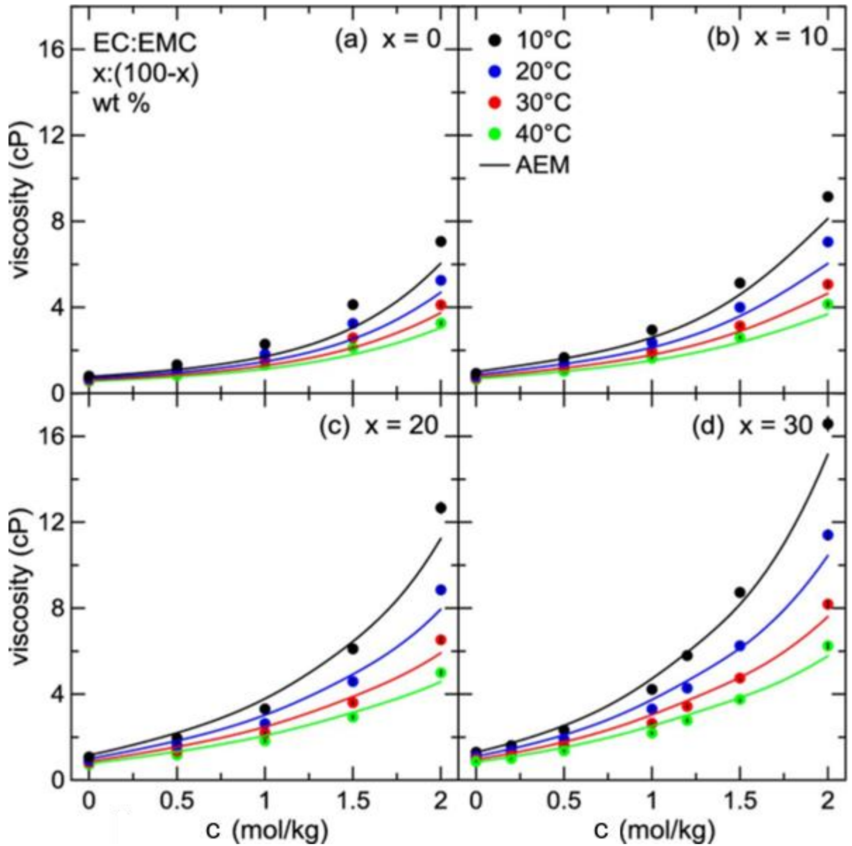
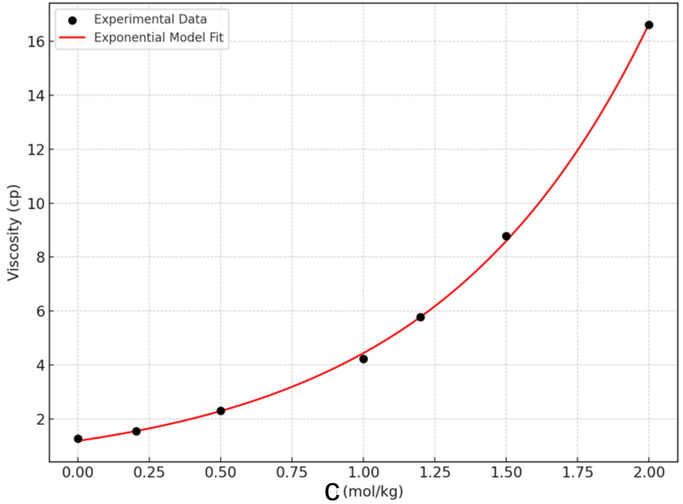
Viscosity of some electrolytes and the effect of salt concentration



10°C LiPF6 + EC:EMC 30:70 Fit



$$\eta = \eta^* e^{Kc}$$

$$\eta^* = 1.18 \quad K = 1.32$$

Talk about D(c)

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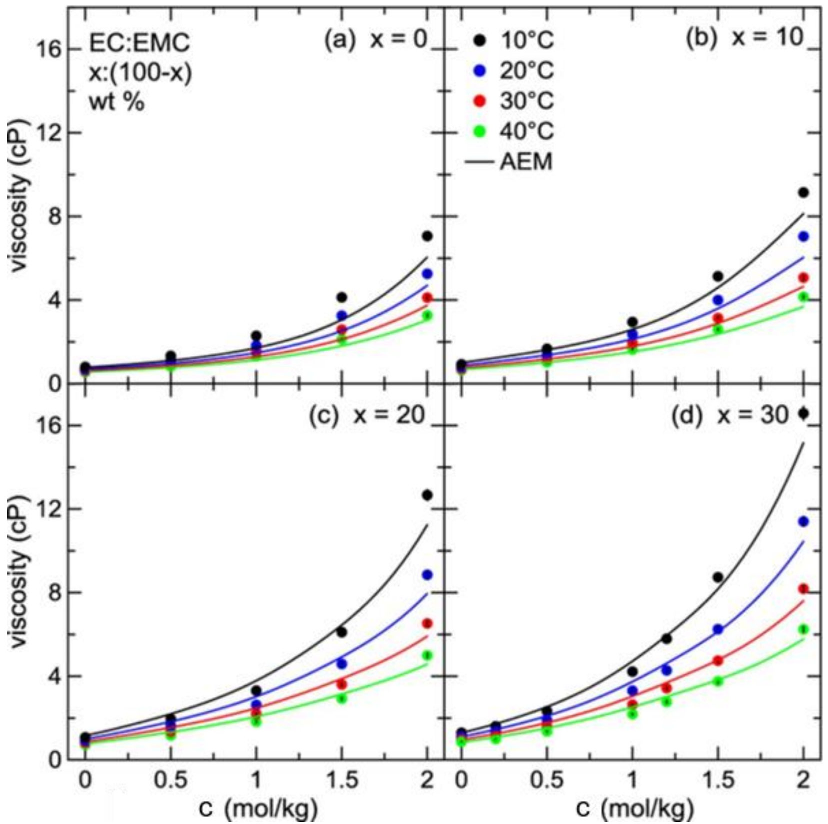
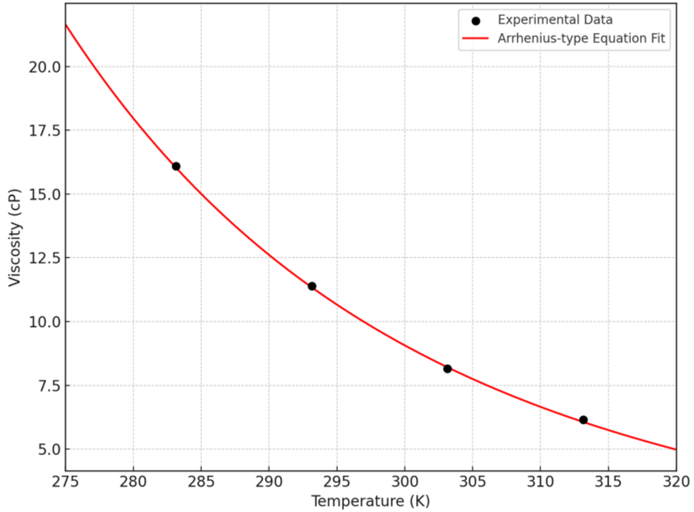
E. R. Logan *et al* 2018 *J. Electrochem. Soc.* **165** A705

Viscosity of some electrolytes and the effect of temperature



2m LiPF6 EC:EMC 30:70 Fit



$$\eta = \eta_0 e^{\frac{E_a}{RT}}$$

Talk about D(T)

$$\eta_0 = 6.31 \cdot 10^{-4} \quad E_a = 0.248$$

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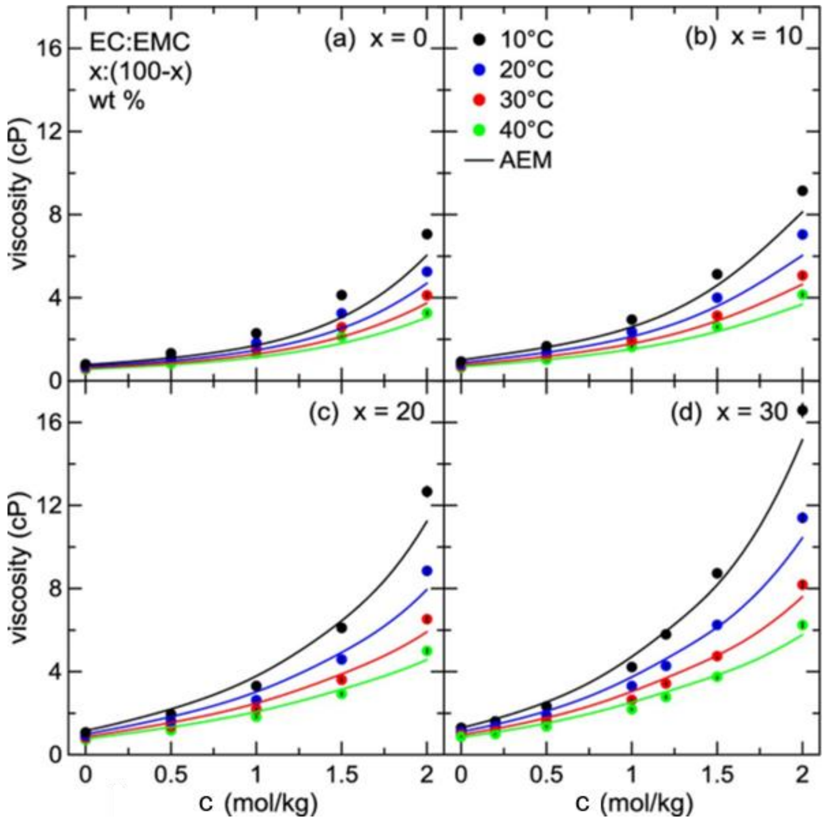
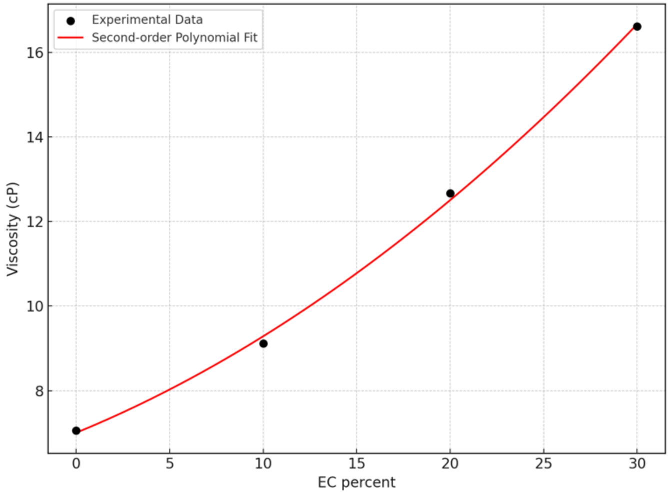
E. R. Logan *et al* 2018 *J. Electrochem. Soc.* **165** A705

Viscosity of some electrolytes and the effect of solvent ratio



2m LiPF6 EC:EMC x:(100-x) 10°C Fit



$$\eta = Ex_{EC}^2 + Fx_{EC} + G$$

(To second order)

E. R. Logan *et al* 2018 *J. Electrochem. Soc.* **165** A705

Which solvent blend would you choose for fast-charging applications at 25°C? Approximate, to first order, η of the mix.

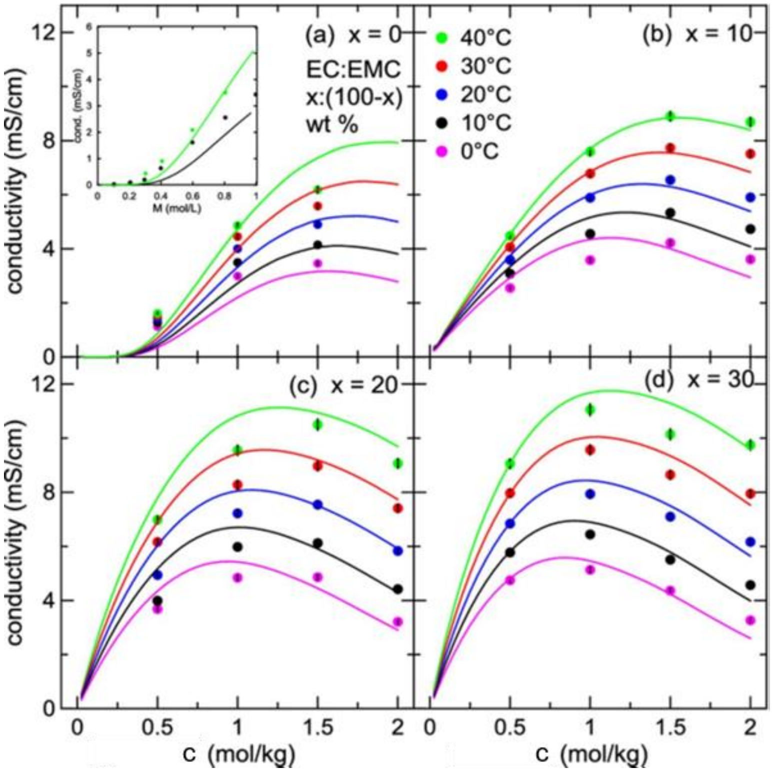
EC:DMC 3:7   EC:DMC:MA 3:5:2   EC:EMC:DMC 25:5:70

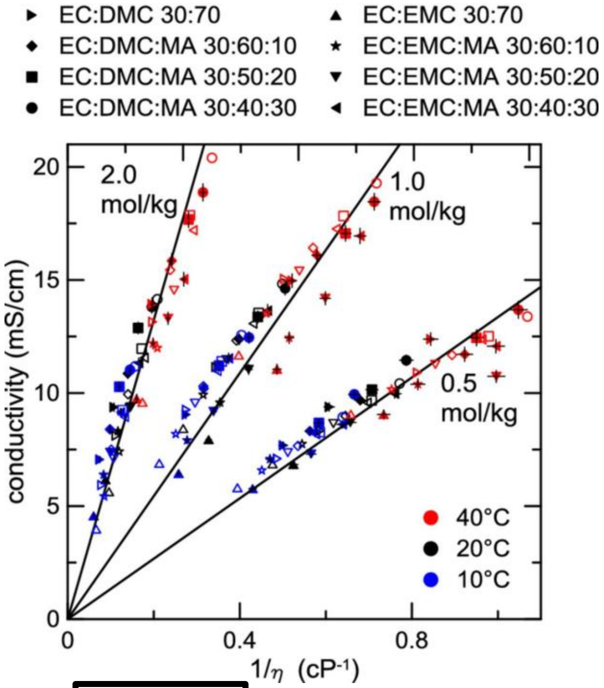
MA: Methyl acetate; η = 0.365 cp at 25°C
EC: Ethylene carbonate; η = 1.9 cp at 40°C (solid at 25°C)
EMC: Ethyl methyl carbonate; η = 0.65 cp at 25°C
DMC: Dimethyl carbonate; η = 0.59 cp at 25°C

Conductivity of some electrolytes (experimental values)

For low EC electrolytes, lower viscosity means lower conductivity. Why?

This is due to lower salt dissociation in the low permittivity of low/free EC electrolytes.





$$\sigma = \frac{kc}{\eta}$$

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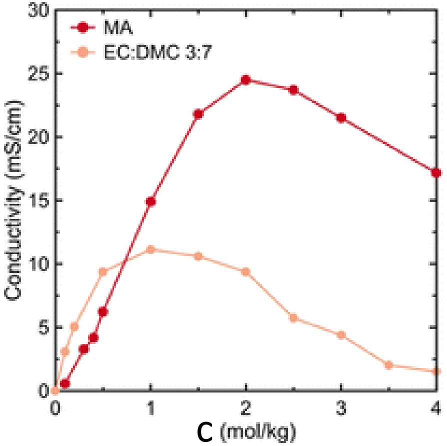
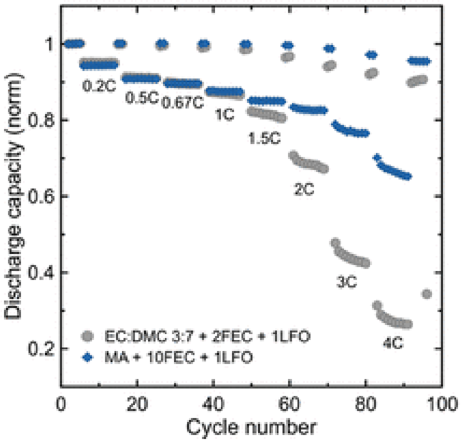
E. R. Logan *et al* 2018 *J. Electrochem. Soc.* **165** A705   https://pubs.acs.org/doi/epdf/10.1021/acsomega.0c03013?ref=article_openPDF

However, challenges to fast charging are present.

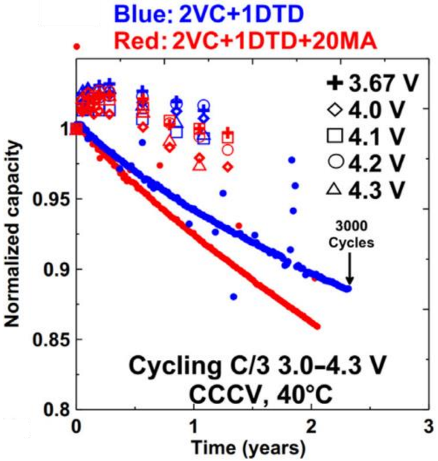
20°C

2 weeks of cycling





40°C



Blue: Electrolyte A

Red: Electrolyte A + 20% Methyl acetate (fast charging additive)

Optimizing the battery for faster charging can result in more degradation in the long term.

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J. Phys. Chem. C 2020, 124, 23, 12269–12280

Trends in Chemistry, April 2020, Vol. 2, No. 4

Electrolyte instability (redox)

Explain this on the board

No electrolyte components that exist are fully stable to reduction and oxidation in a cell.

During a cell's first charge, some of the electrolyte components reduce at the negative electrode, forming the solid electrolyte interface (SEI).

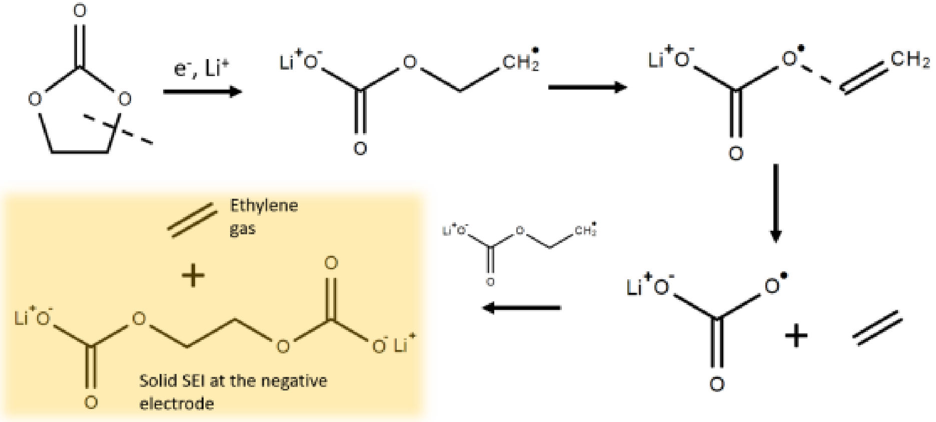
This process irreversibly consumes lithium-ions, resulting in lithium inventory loss and loss of capacity.

The formation of this layer also affects lithium transport at the electrodes, contributing to impedance growth.

A good electrolyte forms a very passivating layer that stops further redox reactions: the SEI.

Electrolyte degradation: Solid electrolyte interface (SEI).

Ethylene carbonate reduce (unwanted) at the negative electrode, forming a thin layer of solid material and gas. Two among many reduction pathway are:



Those reactions consume lithium-ion, resulting in capacity loss.

$$EC + 2\ e^- + 2\ Li^+ \rightarrow Li_2CO_3 + CH_2{=}CH_2$$

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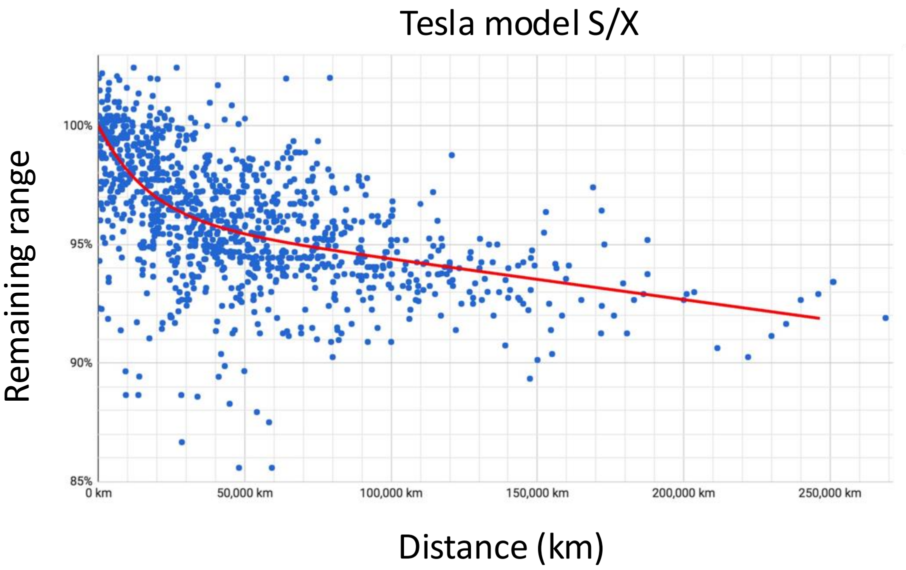
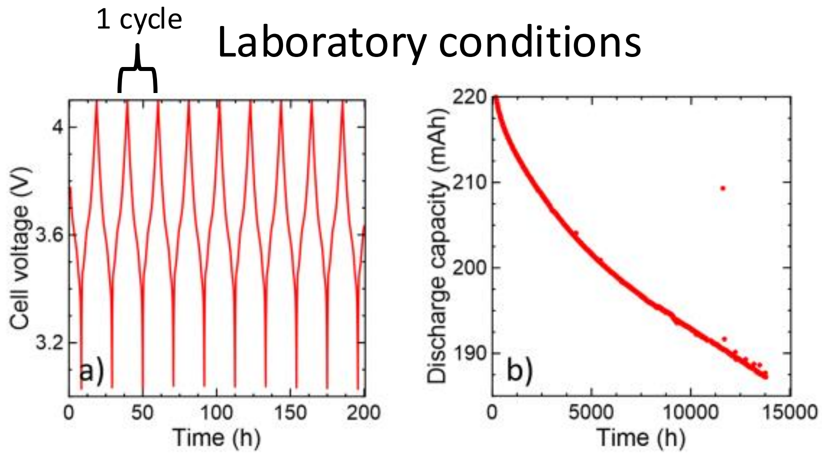
How to measure long-term cell stability?





Lithium inventory loss and capacity loss: $$Q(t) = Q_0(1 - A\sqrt{t})$$

Batteries degrade overtime

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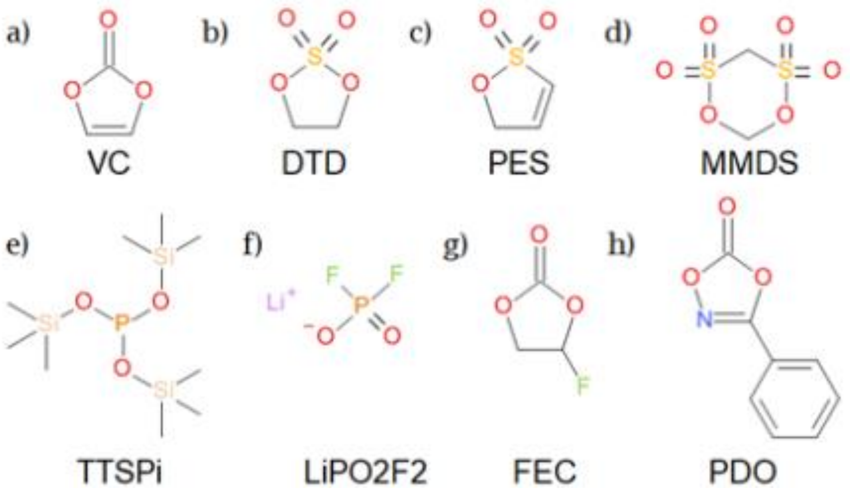
How to improve performance? One solution: Additives

List of some common additives



Most are:

1) Carbonates
2) Organosulfates
3) Phosphates/phosphites,
4) Fluorinated.

Double bonds are also often beneficial

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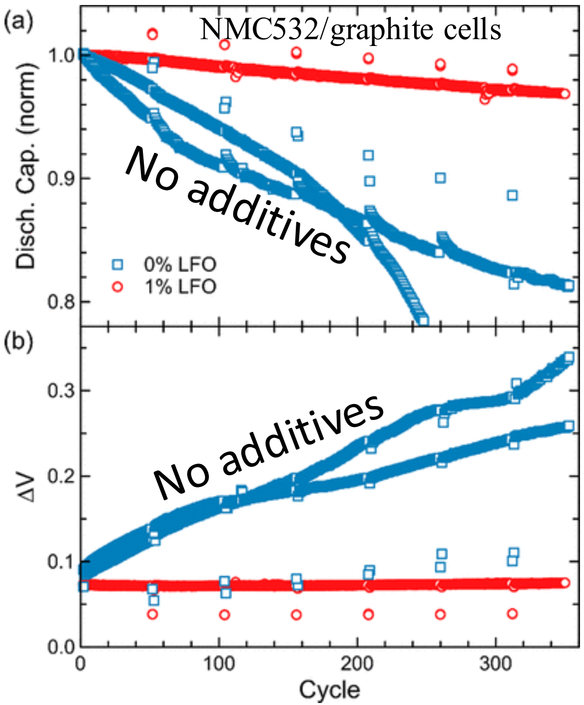
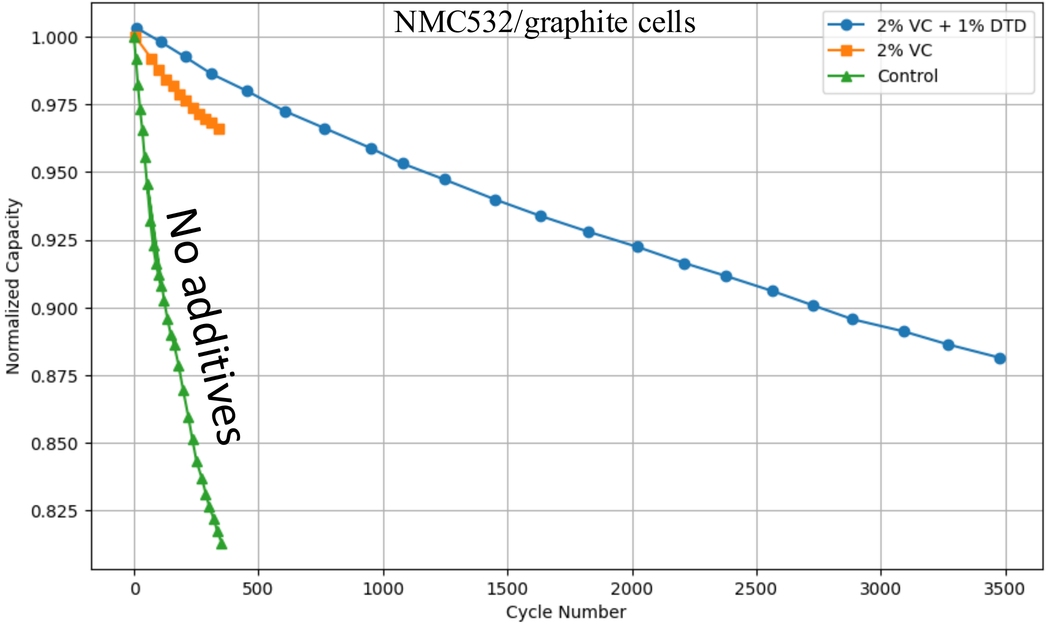
Additives can drastically improve performance



Cycling at 40°C, (C-rate: C/3 (83 mA))

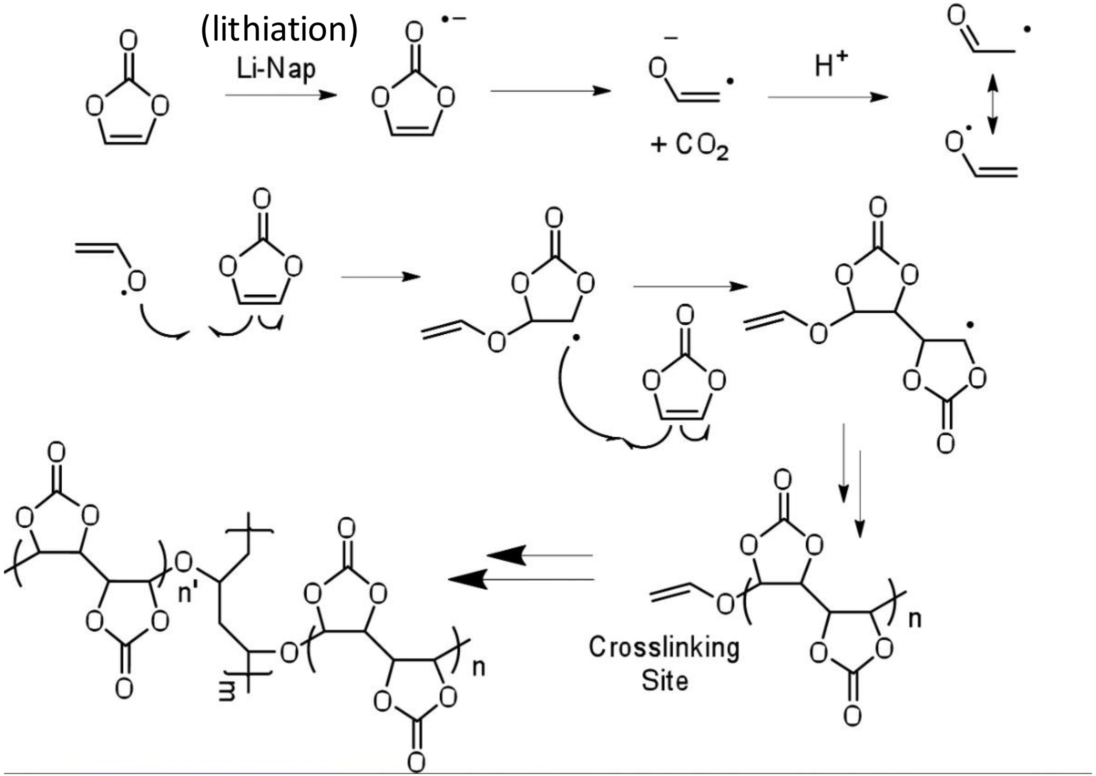


Control: 1.2 M $LiPF_6$ EC:DMC 3:7

ACS Appl. Mater. Interfaces 2019, 11, 15, 14095−14100

J. Electrochem. Soc. 165, A2961–A2967 (2018).

Why do additives improve performance? Some allows the formation of more passivating SEI.



SEI needs to be electrically isolating but ion conductive. SEI stops side reactions while maintaining cell performance.

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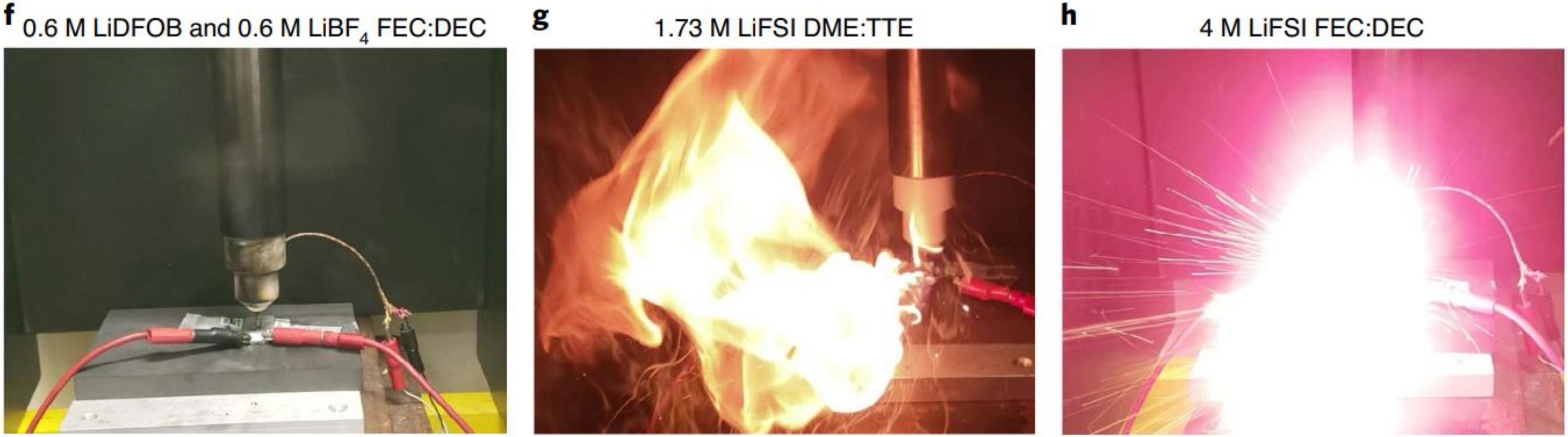
Chem. Mater. 2016, 28, 8149−8159

It is important to always check for safety, not just performance!

A nail test can help with that. Here for a lithium metal battery



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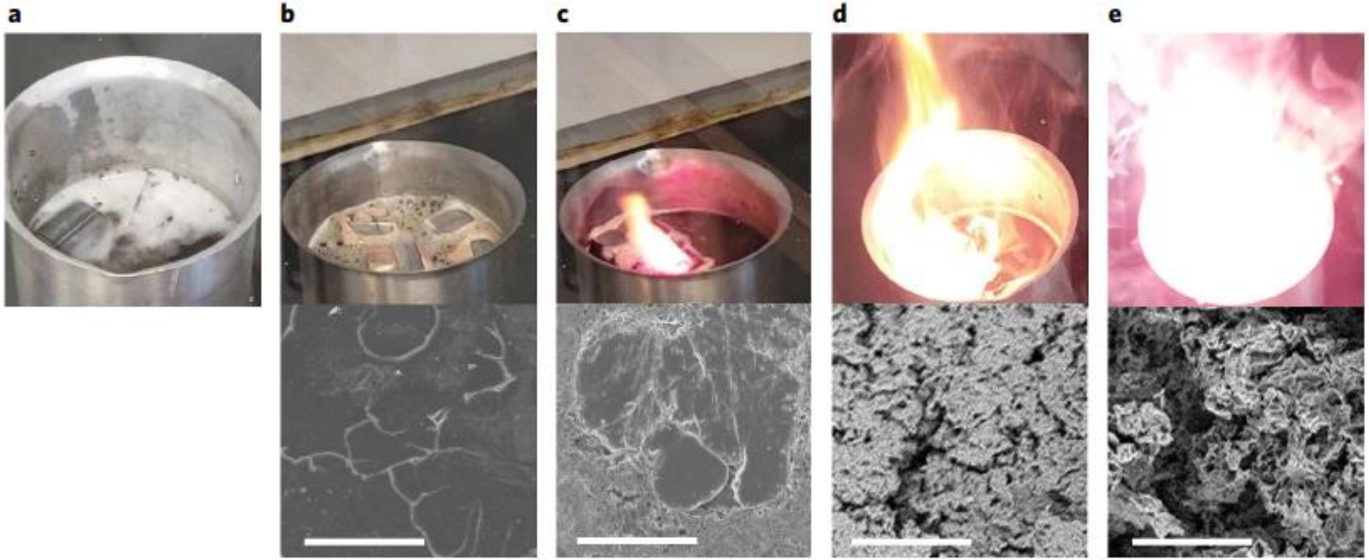
Nature Energy volume 5, pages 693–702 (2020)

Why do some electrolytes increase safety?

In lithium metal-based batteries (anode free and liquid electrolyte based), higher surface area lithium results in worse safety.



Good ion transport favors homogeneous plating, resulting in low surface area. As the cell ages, salt consumption can result in worse transport.
→ Need high conductivity and low rate of salt consumption.

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Nature Energy volume 5, pages 693–702 (2020)

Some reading if you are interested to learn more

1. Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **104**, 4303–4418 (2004).

2. Xu, K. Electrolytes and Interphases in Li-Ion Batteries and Beyond. *Chem. Rev.* **114**, 11503–11618 (2014).

3. Logan, E. A STUDY OF THE TRANSPORT PROPERTIES OF ELECTROLYTES FOR LI-ION BATTERIES. (2018).

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