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Famous quote about safety:

“It will never happen to me”
Captain E.J. Smith (1850 – 1912), Captain of the Titanic

Toxicity Suppression: An Unknown but Highly Appreciable Property of Electrolyte Additives For Safer Batteries

Kubot, M.; Frankenstein, L.; Muschiol, E.; Balke, L.; Klein, S.; Wiemers-Meyer, S.; Nowak, S.; Kasnatscheew, and Martin Winter

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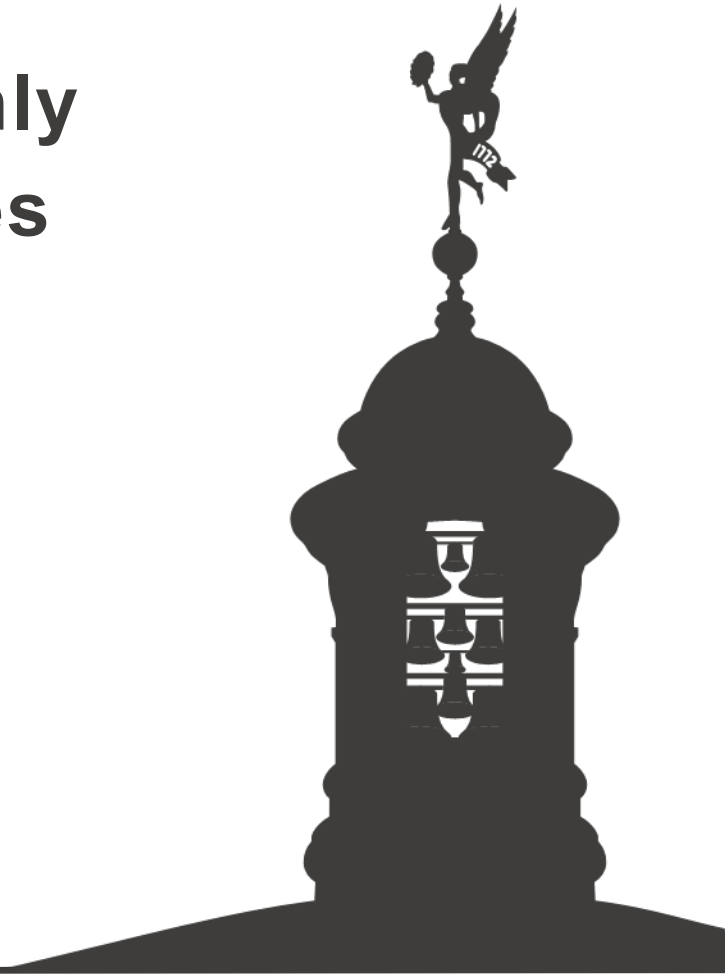

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Acknowledgements

Analytical Investigations

Kubot, Maximilian

Balke, Lisa

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Nowak, Sascha

Toxicity Investigations

Muschiol, Elisabeth

Esselen, Melanie

Cell Chemistry Investigations

Klein, Sven

Frankenstein, Lars

Kasnatscheew, Johannes

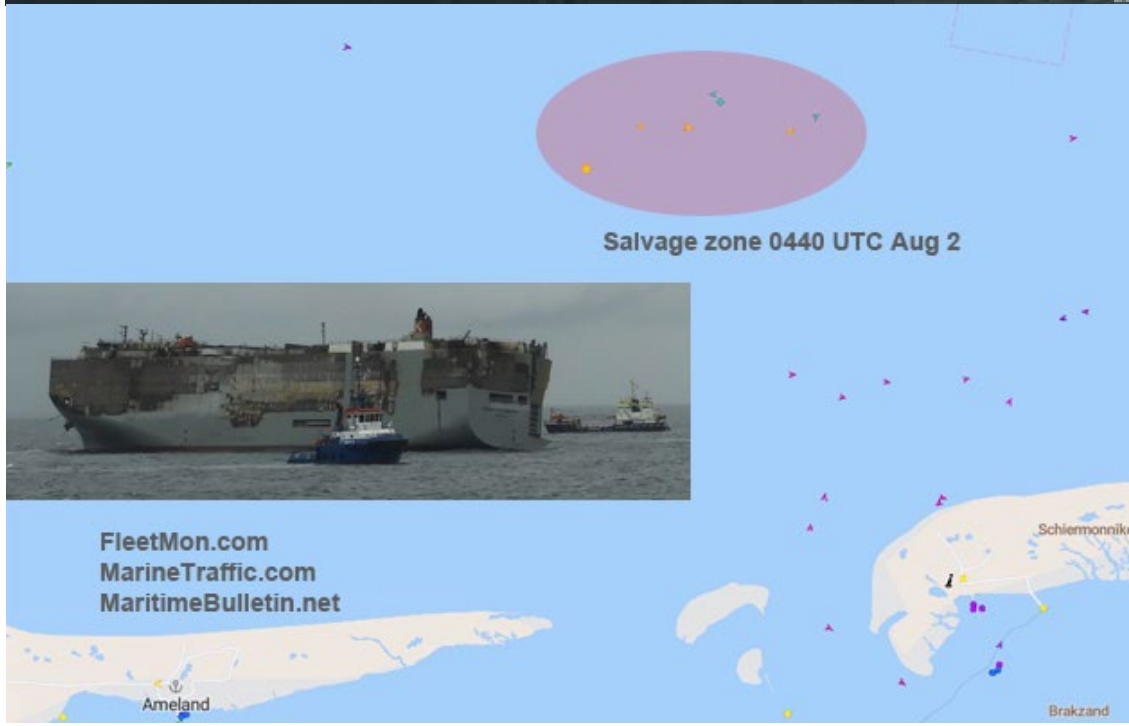
July 26, 2023:

Container Ship “Fremantle Highway” caught fire in the Atlantic, north of NL

-Ship loaded with 3,784 new cars, 498 EVs (LIB powered)

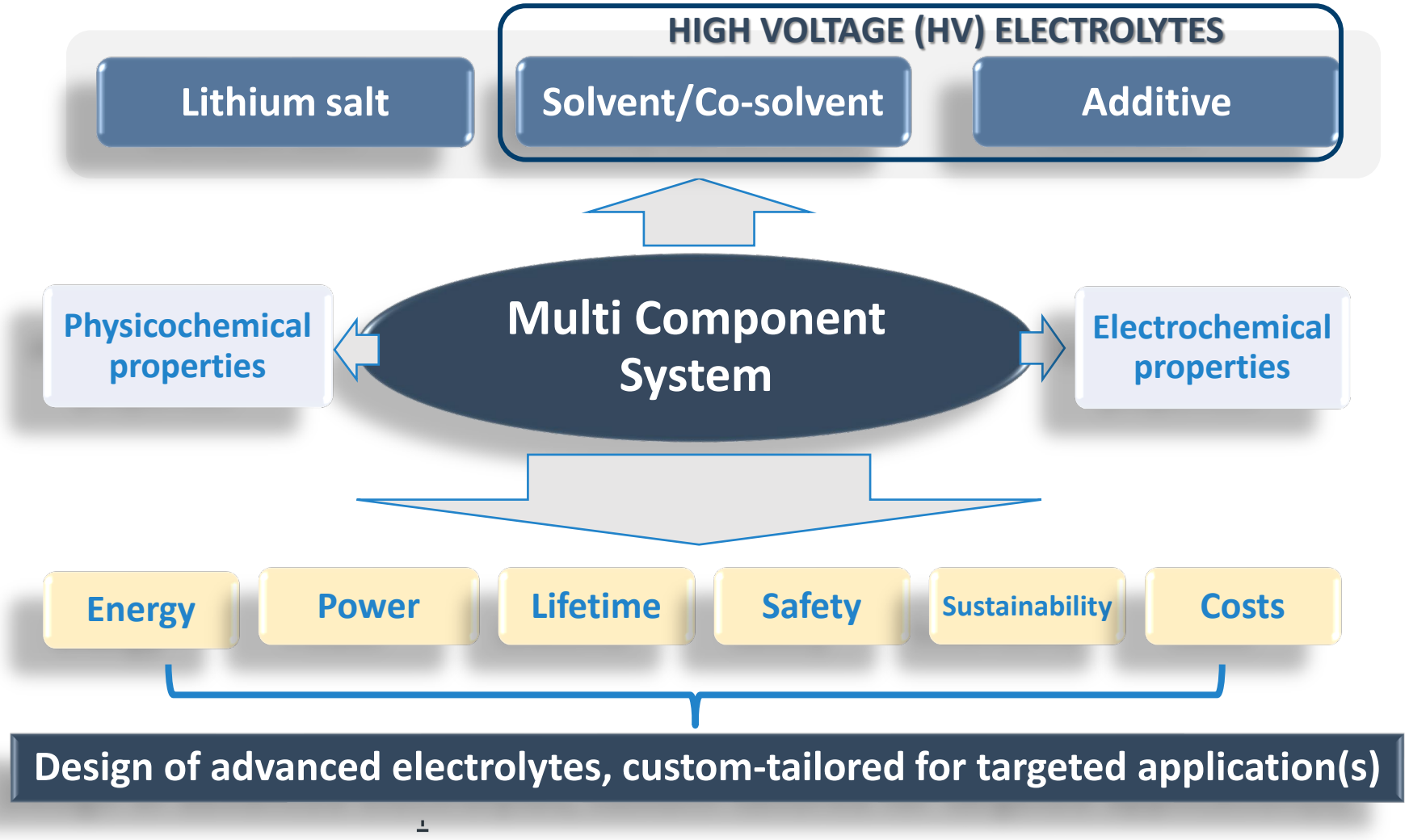
-Concerns that open (burning) LIBs create toxic compounds → environmental disaster

-Cause of fire unknown up to today



https://www.fleetmon.com/maritime-news/2023/42581/car-carrier-evs-major-fire-north-sea-updates-1500-/
https://www.dw.com/en/fremantle-highway-ship-fire-qa/a-66385434
https://www.eurosurveillance.org/content/figure/10.2807/1560-7917.ES.2019.24.15.1800244.f1

Liquid Organic Electrolyte Formulations



- Liquid electrolytes are considered cheaper than solid electrolytes
- Electrolyte and separator: >15% of LIB cell cost
- With a mass fraction of 15-20%, salt costs are up to 85% of electrolyte costs
- Ca. 15-20 US$ per 1 kg of formulated electrolyte
- Electrolytes create additional costs: Filling, formation, etc.

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Angewandte Chemie **2019**, 131, 2

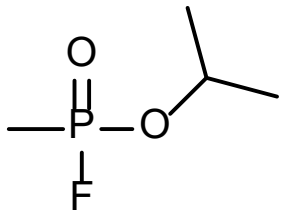
Hydrolysis of the Electrolyte Salt ($LiPF_6$) Results in Toxic Compounds (HF, FPs, and OFPs)

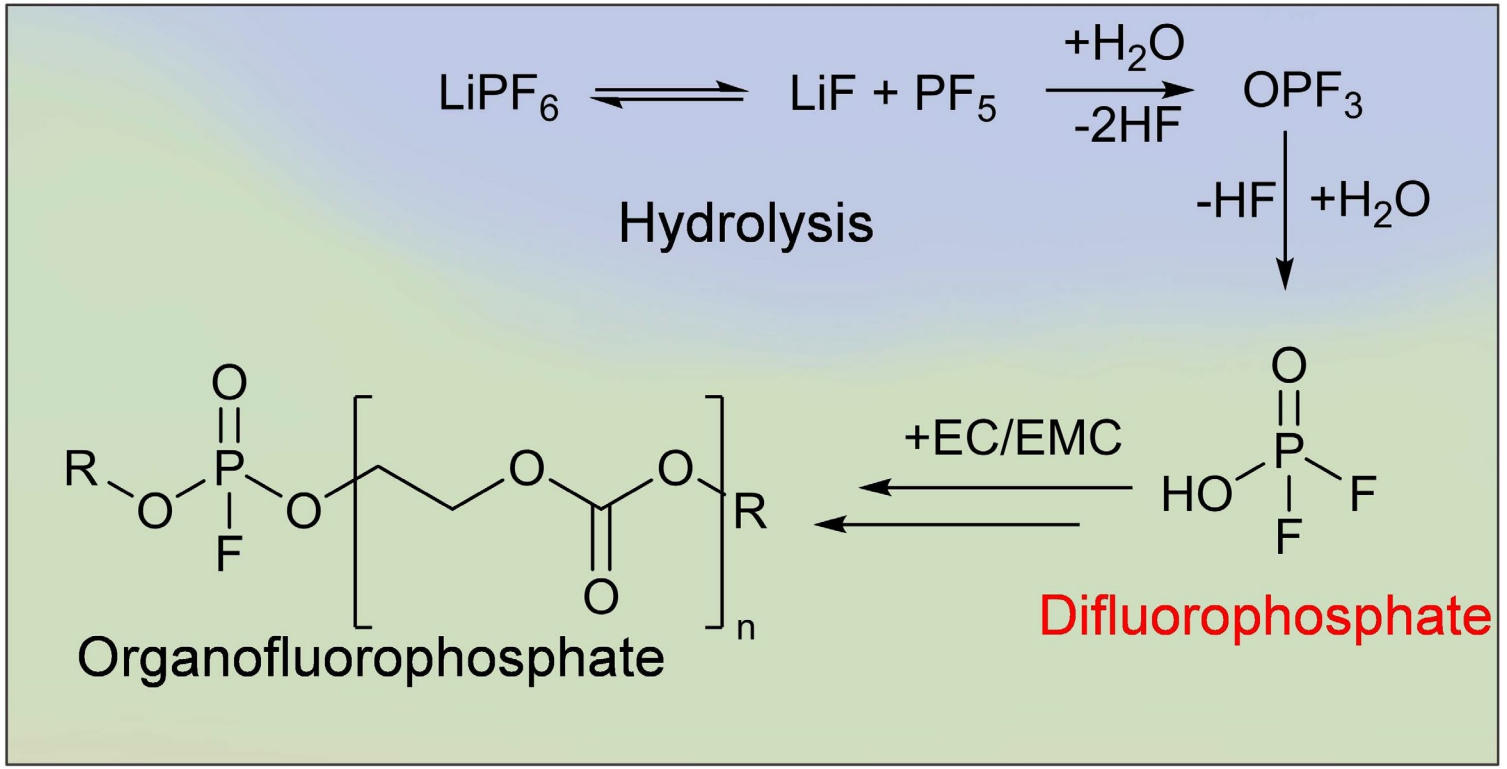
- Hydrofluoric Acid: **HF**
- Fluorophosphates: **FPs**
- Organofluorophosphates: **OFPs**

- OFPs formed by reaction of $LiPF_6$ with organic solvents in presence of water. Higher OFP amounts by:
  - Operation voltage
  - Temperature
  - Life

OFPs: Ca. 40 times more toxic than HF

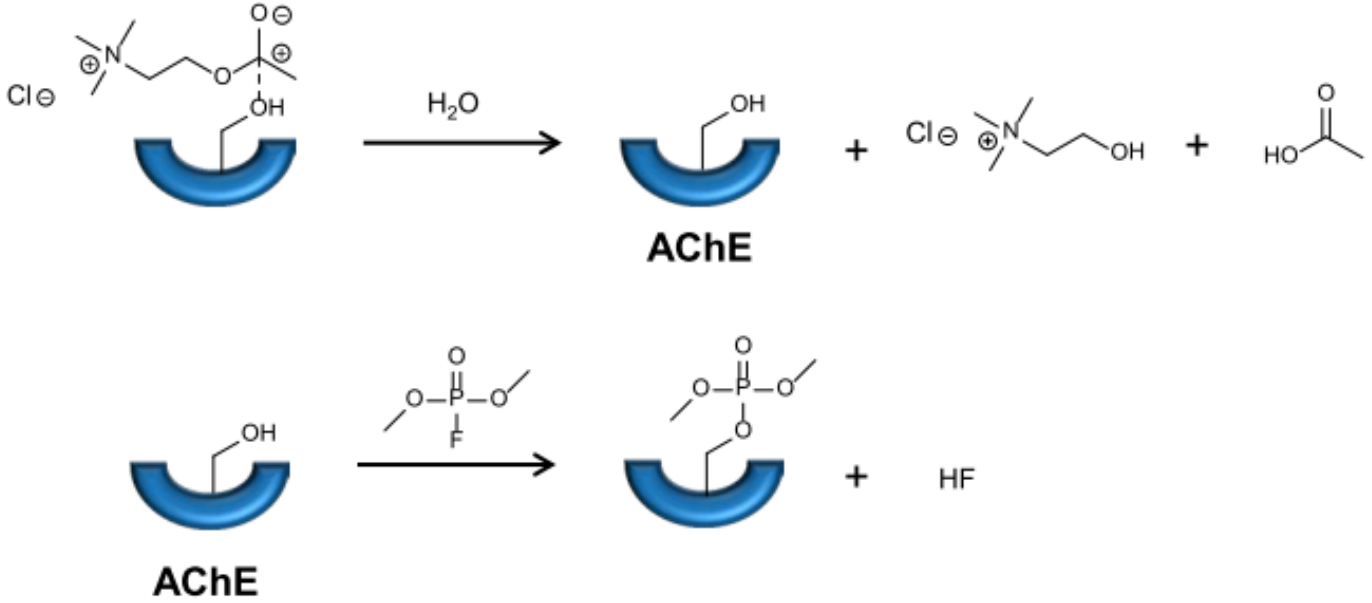
25% of the toxicity of Sarin (chemical warfare)





Kubot, M., Frankenstein, L., Muschiol, E., Klein, S., Esselen, M., Winter, M., Nowak, S., Kasnatscheew, J., *ChemSusChem* 2023, 16, e202202189. .

"The Dose Makes the Poison" *



F. M. Raushel, *Nature* **2011**, *469*, 310-311.

- LD_{50} value: Amount of a solid or liquid material that it takes to kill 50% of test animals in one experiment.
- Roughly: LD50 value of OFPs is exceeded in a 5 kWh battery with standard electrolyte after storage at 80°C for 2 days.

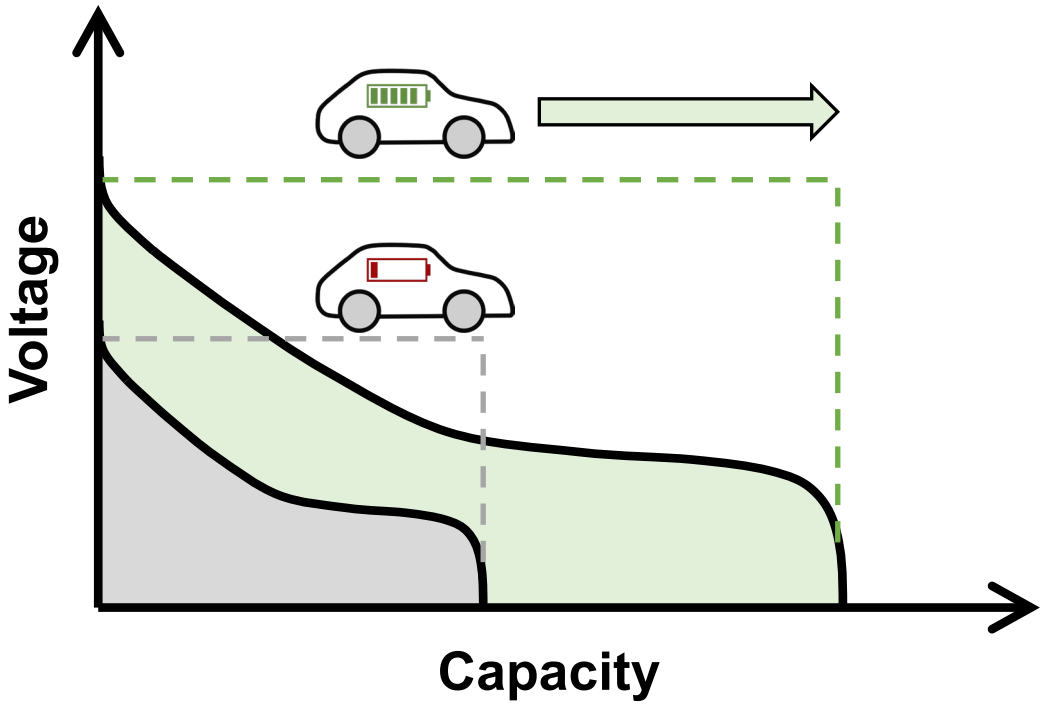
- Acetylcholine chloride is THE important neuro-transmitter between nerve and muscle forming acetylcholine esterase (AChE) after reaction with water (hydrolysis)
- Inhibition of AChE formation by OFPs
  →paralysis, suffocation, decease

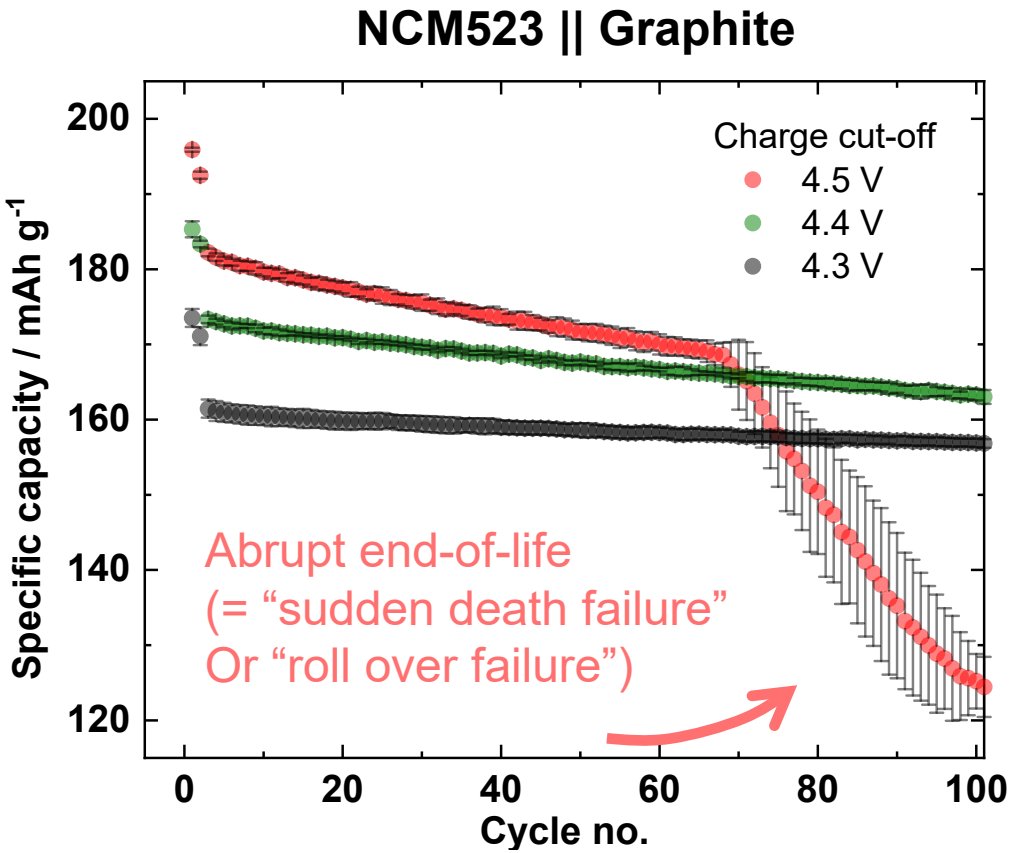
***Paracelsus**
(Philippus Theophrastus Aureolus Bombastus von Hohenheim) Swiss Medic, Alchemist, Theologist, Astrologist and Philosopher, 1493 - 1541

[1] www.lookchem.com (referenced to Journal of Toxicology and Environmental Health 1989, 26, 437), [2] www.lookchem.com (referenced to NTIS (National Technical Information Service))
[3] www.lookchem.com (referenced to Deutsche Gesundheitswesen 1960, 15, 2179), [4] Sigma Aldrich (referenced to RTECS (Registry of Toxic Effects of Chemical Substances))
[5] S. D. Silver, Journal of Industrial Hygiene and Toxicology 1948, 30, 307-311 ; General: S. Nowak, M. Winter, Journal of The Electrochemical Society,

Higher Energy Density LiBs Through Higher Voltage: Cycle Life as Challenge

Energy [Wh] = Voltage [V] x Capacity [Ah]



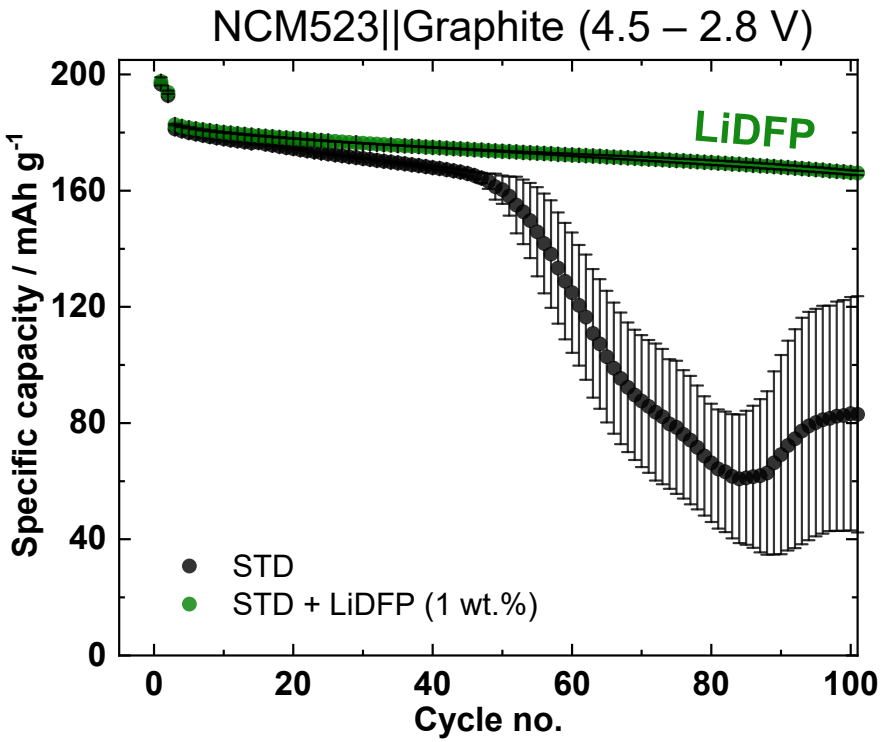


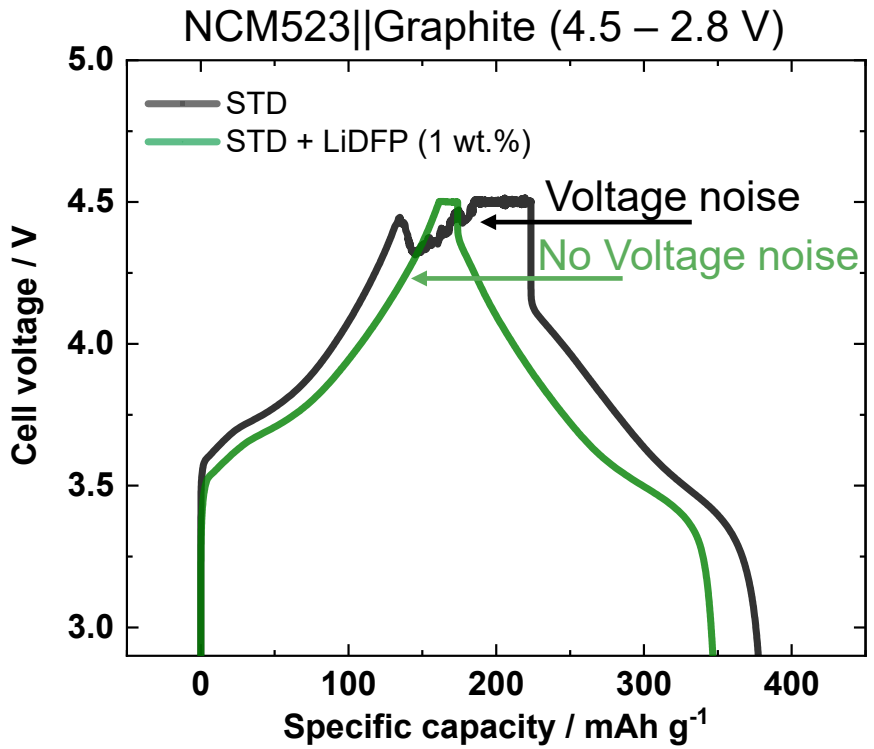
Coin cell: N:P 1.20
Sp. Current: 90 mA g^{-1} (≈ 0.5 C)
Electrolyte: 1 M $LiPF_6$ in EC:EMC (3:7 by wt.) soaked in Celgard ® separator

S. Klein, P. Bärmann, L. Stolz, K. Borzutzki, J.-P. Schmiegel, M. Börner, M. Winter, T. Placke, J. Kasnatscheew *ACS Applied Materials & Interfaces*. **2021**, 13, 57241-57251.

Lithium Fluorophosphates ($Li_xPO_yF_z$) as Commercial Electrolyte Additive in STD Electrolyte

Cycle No. 50:





- → LiDFP is soluble in electrolyte.
- → No rollover failure with LiDFP.
- → LiDFP has also a positive effect at lower cut-off voltages
- → Other additives show not the same performance

Coin cell: N:P 1.20
Sp. Current: 90 mA g^{-1} (≈ 0.5 C)
Electrolyte: 1 M $LiPF_6$ in EC:EMC (3:7 by wt.) + X soaked in Celgard ® separator

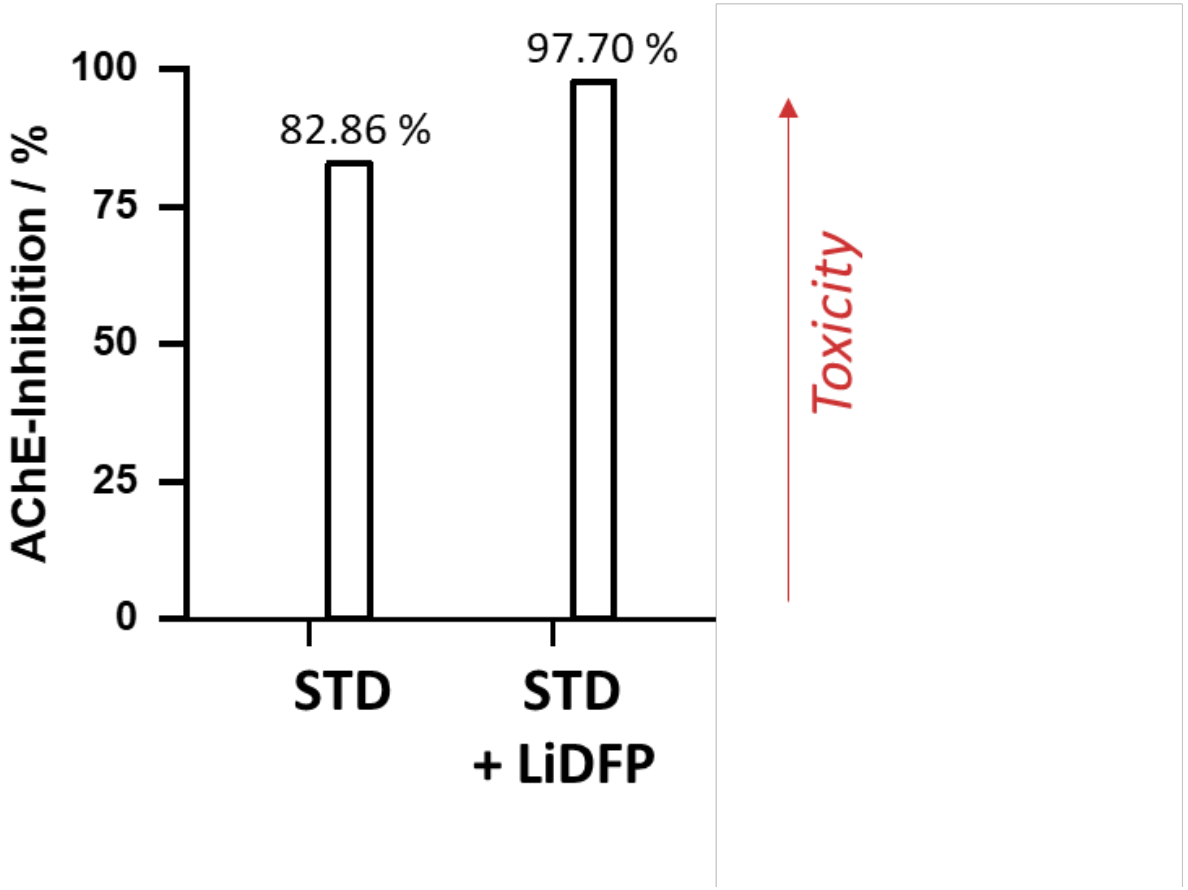
S. Klein, P. Harte, S. van Wickeren, K. Borzutzki, S. Röser, P. Bärmann, S. Nowak, M. Winter, T. Placke, J. Kasnatscheew *Cell Reports Physical Science*. **2021**, 2, 100521.

Lithium Difluorophosphates (*e.g.*, LiDFP) Form OFPs and Are Thus More Toxic than STD Electrolyte

Inhibition of acetylcholinesterase (AChE) formation allows quantification

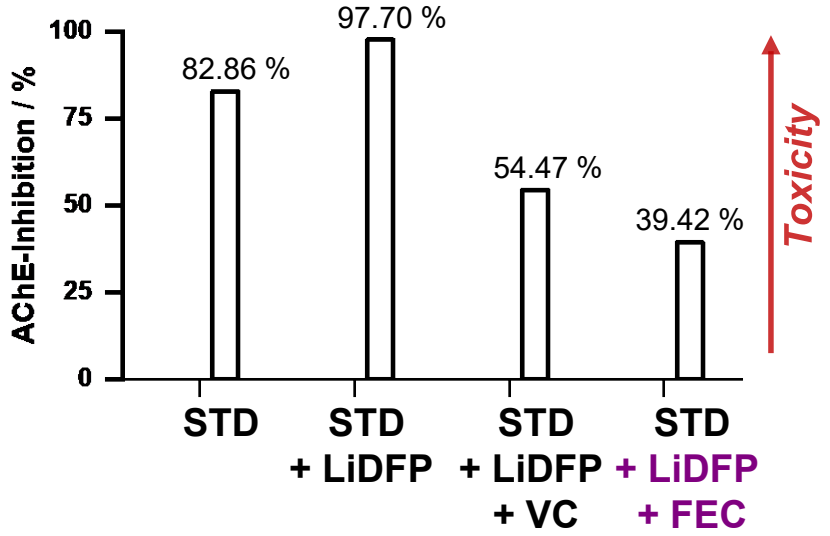
(a) High performance liquid chromatography (HPLC) after 7 days storage of STD electrolyte + 1wt.% LiDFP at 80 °C

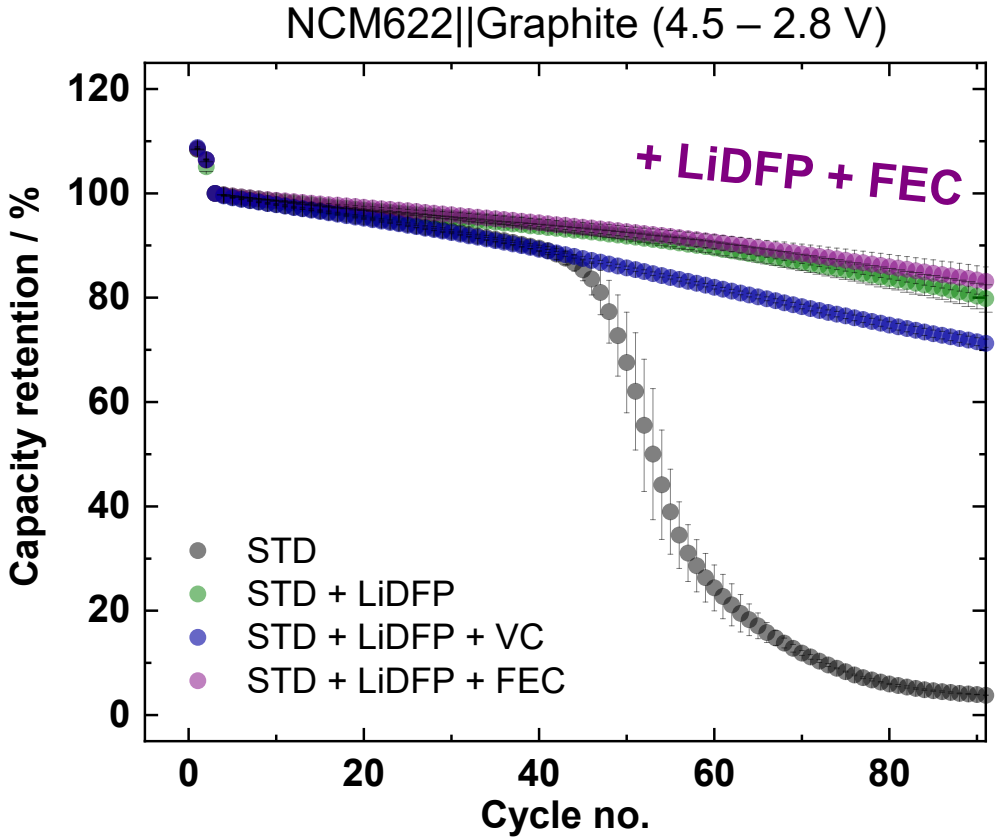
(b) Acetylcholinesterase (AChE) as literature-known measure for toxicity determination of organofluorophosphates



Kubot, M., Frankenstein, L., Muschiol, E., Klein, S., Esselen, M., Winter, M., Nowak, S., Kasnatscheew, J., *ChemSusChem* **2023**, 16, e202202189.
Hammond P. S:, Forster J. S., Anal. Biochem. **1989**, 180, 380–383.

LiDFP: Dual-Additive Approach with Fluoroethylene Carbonate (FEC) or Vinylene Carbonate (VC)



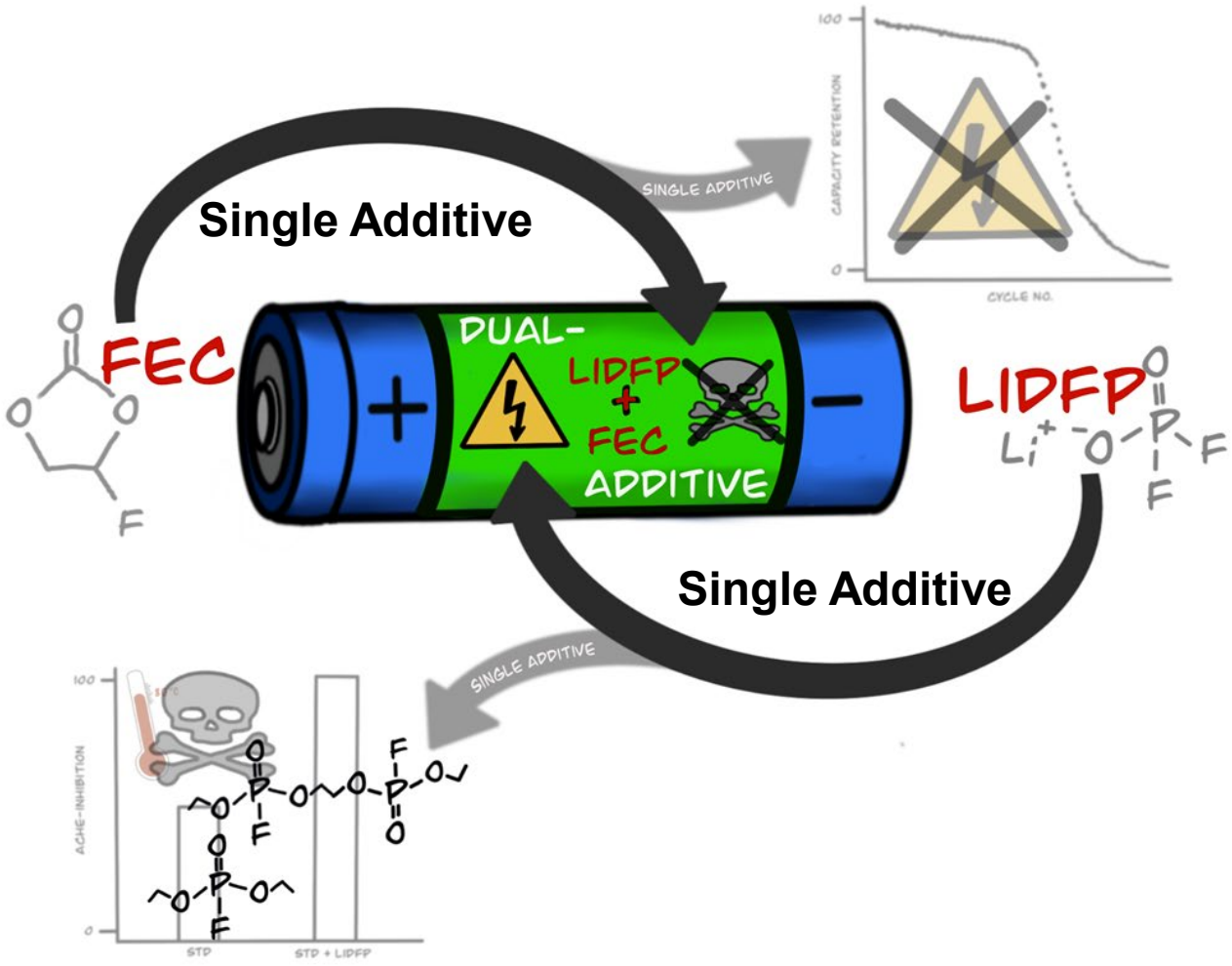


- Additives VC and FEC create “cross-linked” and thus more robust interphases (SEI and CEI)
- Fluorophosphates (LiDFP) react with electrolyte. Preferred reaction with electrolyte additives.
- As a consequence, OFPs are incorporated in SEI/CEI and do not stay in solution.

Coin cell: N:P 1.20, Sp. Current: 178 mA g^{-1} (≈ 1.0 C)
Electrolyte: 1 M $LiPF_6$ in EC:EMC (3:7 by wt.) soaked in Celgard ® separator

Kubot, M., Frankenstein, L., Muschiol, E., Klein, S., Esselen, M., Winter, M., Nowak, S., Kasnatscheew, J., *ChemSusChem* 2023, 16, e202202189. .

Multiple Additive Approach: Enhancement of Performance and Safety



Dual additive approach is a blessing for safety and performance

- **Toxicity suppression**
- **Cycling performance improvement**

Kubot, M; Balke, L; Scholz, J; Wiemers-Meyer, S; Karst, U; Hayen, H; Hur, H; Winter, M; Kasnatscheew J; Nowak, S. 2023. *Advanced Science,* 2024,11, 2305282

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meet

“Luck is a very thin wire between survival and disaster, and not many people can keep their balance on it.”

Hunter Stockton Thompson (1937 – 2005), American journalist and author