U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

Fluorinated Materials for Battery Electrolytes: Enablers & Key Challenges

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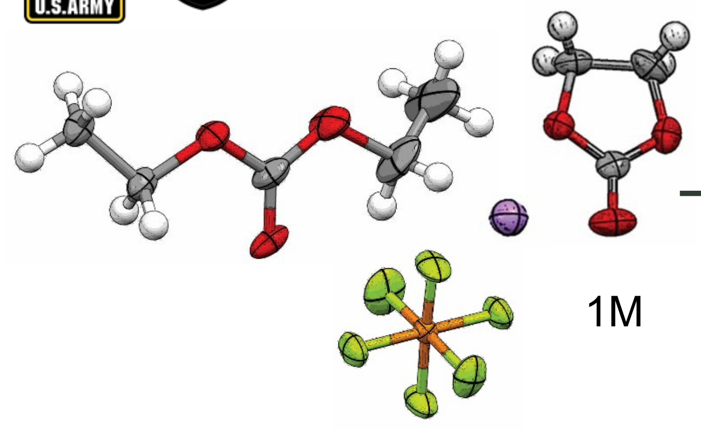
POC: Wesley Henderson, 331-316-6637

Fluorinated Materials: Enablers

Highly Concentrated Electrolytes (HCEs)



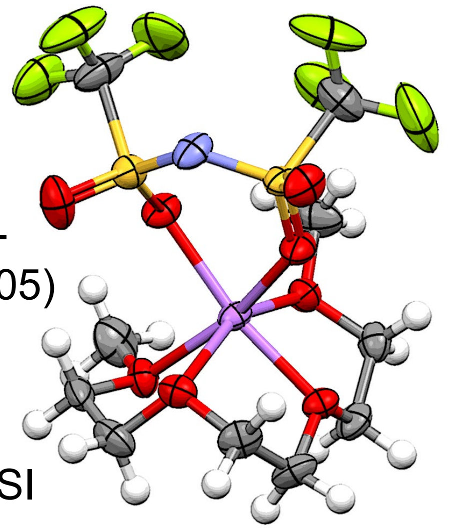
1M

S.-K. Jeong, H.-Y. Seo, D.-H. Kim, H.-K. Han, J.-G. Kim, Y. B. Lee, Y. Iriyama, T. Abe, and Z. Ogumi, *Electrochem. Commun.*, **10**, 635 (2008).

Y. Yamada, Y. Takazawa, K. Miyazaki, and T. Abe, *J. Phys. Chem. C*, **114**, 11680 (2010).

> 3M

Glyme-LiX Electrolytes – Henderson (2001 - 2005)



(G3)$_1$:LiTFSI

W. A. Henderson, Ph.D. Thesis, University of Minnesota (2001).

T. M. Pappenfus, W. A. Henderson, B. B. Owens, K. R. Mann, and W. H. Smyrl, *J. Electrochem. Soc.*, **151**, A209 (2004).

W. A. Henderson, F. McKenna, M. A. Khan, N. R. Brooks, V. G. Young Jr., and R. Frech, *Chem. Mater.*, **17**, 2284 (2005).

“**Solvate Ionic Liquids** (**SILs**)” – **Watanabe Group** (2008 -)

(G3)$_n$-LiTFSI (n = 1)
(G4)$_n$-LiTFSI (n = 1)

triglyme (G3)
tetraglyme (G4)

M. Nakamura, Y. Kazue, S. Seki, K. Dokko, and M. Watanabe, 214th Electrochemical Society Meeting, Abstract #742, MA2008-02 742 (2008).

K. Yoshida, M. Nakamura, Y. Kazue, K. Dokko, and M. Watanabe, 214th Electrochemical Society Meeting, Abstract #3022, MA2008-02 3022 (2008).

T. Tamura, T. Hachida, K. Yoshida, N. Tachikawa, K. Dokko, and M. Watanabe, *J. Power Sources*, **195**, 6095 (2010).

T. Tamura, K. Yoshida, T. Hachida, M. Tsuchiya, M. Nakamura, Y. Kazue, N. Tachikawa, K. Dokko, and M. Watanabe, *Chem. Lett.*, **39**, 753 (2010).

K. Yoshida, M. Nakamura, Y. Kazue, N. Tachikawa, S. Tsuzuki, S. Seki, K. Dokko, and M. Watanabe, *J. Am. Chem. Soc.*, **133**, 13121 (2011).

“**Highly Concentrated Electrolytes** (**HCEs**)” (2013 -)

L. Suo, Y.-S. Hu, H. Li, M. Armand, and L. Chen, *Nat. Commun.*, **4**, 1481 (2013).

K. Matsumoto, K. Inoue, K. Nakahara, R. Yuge, T. Noguchi, and K. Utsugi, *J. Power Sources*, **231**, 234 (2013).

Y. Yamada, M. Yaegashi, T. Abe, and A. Yamada, *Chem. Commun.*, **49**, 11194 (2013).

M. Nie, D. P. Abraham, D. M. Seo, Y. Chen, A. Bose, and B. L. Lucht, *J. Phys. Chem. C*, **117**, 25381 (2013).

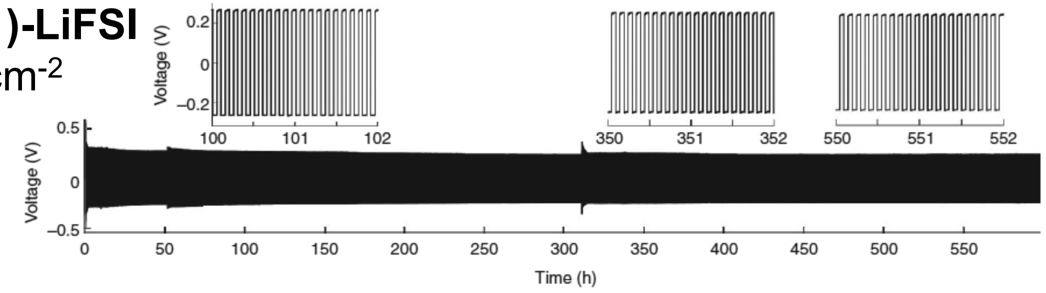
D. W. McOwen, D. M. Seo, O. Borodin, P. D. Boyle, and W. A. Henderson, *Energy Environ. Sci.*, **7**, 416 (2014).

J. Qian, W. A. Henderson, W. Xu, P. Bhattacharya, M. Engelhard, O. Borodin, and J.-G. Zhang, *Nat. Comm.*, **6**, 6362 (2015).

…and many more…

High Rate and Stable Cycling of Lithium Metal Anode (cited: 1763)

4M DME (G1)-LiFSI
10 mA cm^{-2}



Localized Highly Concentrated Electrolytes (LHCEs)

K. Naoi, E. Iwama, N. Ogihara, Y. Nakamura, H. Segawa, and Y. Inob, *J. Electrochem. Soc.*,**156**, A272 (2009).

K. Naoi, E. Iwama, Y. Honda, F. Shimodate, *J. Electrochem. Soc.*, **157**, A190 (2010).

G. Nagasubramanian and C. J. Orendorff, *J. Power Sources*, **196**, 8604 (2011).

"Solvate Ionic Liquids (SILs)" + **Fluorinated Ethers**

– Watanabe Group (2013 -)

K. Dokko, N. Tachikawa, K. Yamauchi, M. Tsuchiya, A. Yamazaki, E. Takashima, J.-W. Park, K. Ueno, S. Seki, N. Serizawa, and M. Watanabe, *J. Electrochem. Soc.*, **160**, A1304 (2013).

H. Moon, T. Mandai, R. Tatara, K. Ueno, A. Yamazaki, K. Yoshida, S. Seki, K. Dokko, and M. Watanabe, *J. Phys. Chem. C*, **119**, 3957 (2015).

K. Ikeda, S. Terada, T. Mandai, K. Ueno, K. Dokko, and M. Watanabe, *Electrochemistry*, **83**, 914 (2015).

S. Saito, H. Watanabe, K. Ueno, T. Mandai, S. Seki, S. Tsuzuki, Y. Kameda, K. Dokko, M. Watanabe, and Y. Umebayashi, *J. Phys. Chem. B*, **120**, 3378 (2016).

K. Ueno, J. Murai, K. Ikeda, S. Tsuzuki, M. Tsuchiya, R. Tatara, T. Mandai, Y. Umebayashi, K. Dokko, and M. Watanabe, *J. Phys. Chem. C*, **120**, 15792 (2016).

K. Ueno, J. Murai, H. Moon, K. Dokko, and M. Watanabe, *J. Electrochem. Soc.*, **164**, A6088 (2017).

K. Takahashi, Y. Ishino, W. Murata, Y. Umebayashi, S. Tsuzuki, M. Watanabe, H. Takaba, and S. Seki, *RSC Adv.*, **9**, 24922 (2019).

"Highly Concentrated Electrolytes (HCEs)" (2013 -)

L. Suo, Y.-S. Hu, H. Li, M. Armand, and L. Chen, *Nat. Commun.*, **4**, 1481 (2013).

K. Matsumoto, K. Inoue, K. Nakahara, R. Yuge, T. Noguchi, and K. Utsugi, *J. Power Sources*, **231**, 234 (2013).

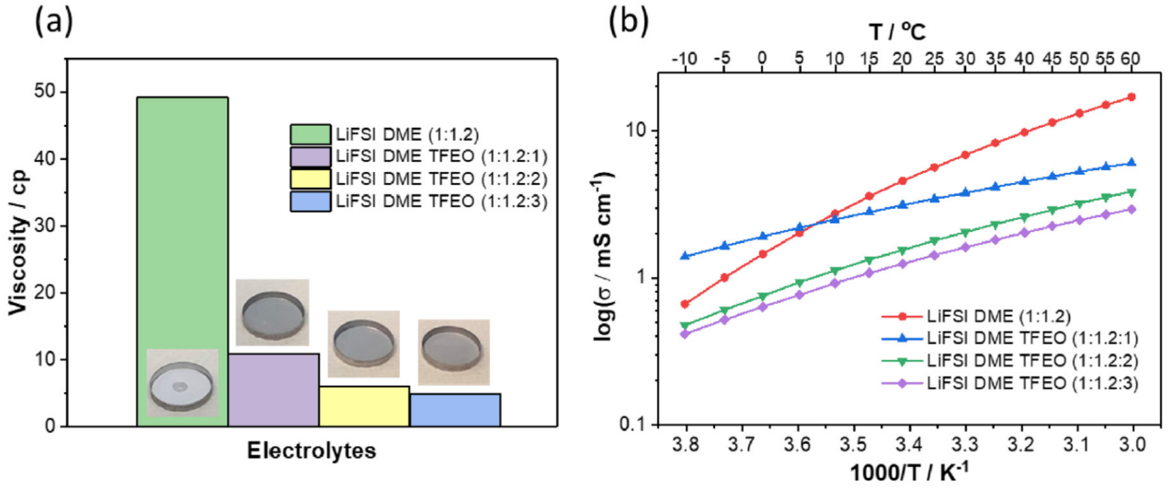
Y. Yamada, M. Yaegashi, T. Abe, and A. Yamada, *Chem. Commun.*, **49**, 11194 (2013).

M. Nie, D. P. Abraham, D. M. Seo, Y. Chen, A. Bose, and B. L. Lucht, *J. Phys. Chem. C*, **117**, 25381 (2013).

D. W. McOwen, D. M. Seo, O. Borodin, P. D. Boyle, and W. A. Henderson, *Energy Environ. Sci.*, **7**, 416 (2014).

J. Qian, W. A. Henderson, W. Xu, P. Bhattacharya, M. Engelhard, O. Borodin, and J.-G. Zhang, *Nat. Comm.*, **6**, 6362 (2015).

…and many more…



"Localized Highly Concentrated Electrolytes (LHCEs)" (2018 -)

S. Chen, J. Zheng, L. Yu, X. Ren, M. H. Engelhard, C. Niu, H. Lee, W. Xu, J. Xiao, J. Liu, and J.-G. Zhang, *Joule*, **2**, 1548 (2018).

S. Chen, J. Zheng, D. Mei, K. S. Han, M. H. Engelhard, W. Zhao, W. Xu, J. Liu, and J.-G. Zhang, *Adv. Mater.*, **30**, 1706102 (2018).

S. P. Beltran, X. Cao, J.-G. Zhang, and P. B. Balbuena, *Chem. Mater.*, **32**, 5973 (2020).

X. Cao, H. Jia, W. Xu, and J.-G. Zhang, *J. Electrochem. Soc.*, **168**, 010522 (2021).

Y. Zheng and P. B. Balbuena, *J. Chem. Phys.*, **154**, 104702 (2021).

X. Cao, P. Gao, X. Ren, L. Zou, M. H. Engelhard, B. E. Matthews, J. Hu, C. Niu, D. Liu, B. W. Arey, C. Wang, J. Xiao, J. Liu, W. Xu, and J.-G. Zhang, *Proc. Nat. Acad. Sci.*, **118**, e2020357118 (2021).

X. Cao, L. Zou, B. E. Matthews, L. Zhang, X. He, X. Ren, M. H. Engelhard, S. D. Burton, P. Z. El-Khoury, H.-S. Lim, C. Niu, H. Lee, C. Wang, B. W. Arey, C. Wang, J. Xiao, J. Liu, W. Xu, and J.-G. Zhang, *Energy Storage Mater.*, **34**, 76 (2021).

F. Ren, Z. Li, J. Chen, P. Huguet, Z. Peng, and S. Deabate, *ACS Appl. Mater. Interfaces*, **14**, 4211 (2022).

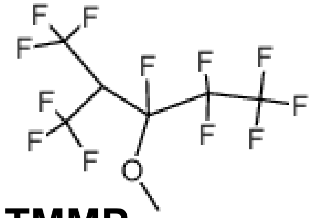
E. Huangzhang, X. Zeng, T. Yang, H. Liu, C. Sun, Y. Fan, H. Hu, X. Zhao, X. Zuo, and J. Nan, *Chem. Engr. J.*, **439**, 135534 (2022).

Battery500 Project

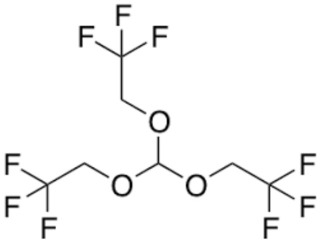
LHCEs: Fluorinated Solvents (Hydrofluoroethers (HFEs))

HFEs: Engineering Fluids

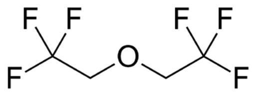
- Designed for heat transfer applications
- Developed originally as a replacement for chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) and perfluorocarbons (PFCs)
- Low(er) Climate Change impact



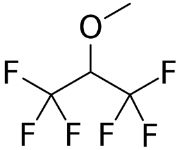
TMMP
NA g cm^{-3}
bp: NA
fp: NA
FW: 332.09



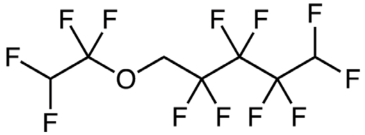
TFEO
1.46 g cm^{-3}
bp: 144-146^{o}C
fp: 60^{o}C
FW: 310.11



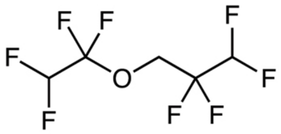
BTFE
1.40 g cm^{-3}
bp: 61-62^{o}C
fp: 1^{o}C
FW: 182.06



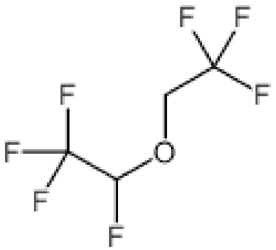
HFME
1.39 g cm^{-3}
bp: 50^{o}C
fp: >93^{o}C
FW: 182.06



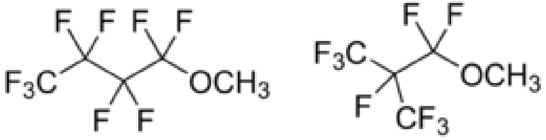
OFE
1.66 g cm^{-3}
bp: 133^{o}C
fp: 45^{o}C
FW: 332.09



TTE
1.53 g cm^{-3}
bp: 93^{o}C
fp: 27^{o}C
FW: 232.07



TFTEOE
1.40 g cm^{-3}
bp: 56^{o}C
fp: NA
FW: 200.06



MFE (mixture of isomers)
1.52 g cm^{-3}
bp: 61^{o}C
fp: NA
FW: 250.06

TMMP: 2-trifluoromethyl-3-methoxyperfluoropentane

TPTP: 2-trifluoro-2-fluoro-3-difluoropropoxy-3-difluoro-4-fluoro-5-trifluoropentane

OFE: 1*H*,1*H*,5*H*-octafluoropentyl 1,1,2,2-tetrafluoroethyl ether

TFEO: tris(2,2,2-trifluoroethyl)orthoformate

TTE: 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether

BTFE: bis(2,2,2−trifluoroethyl) ether

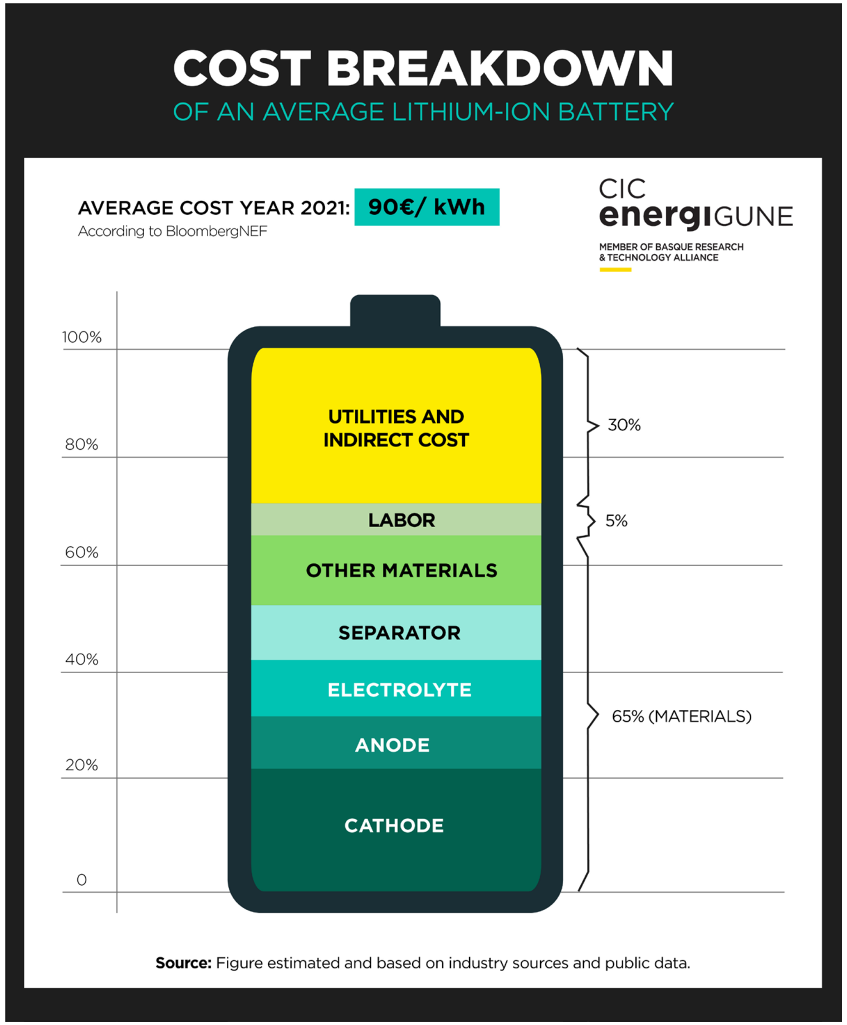
HFME: hexafluoroisopropyl methyl ether

TFTEOE: tetrafluoro−1−(2,2,2−trifluoroethoxy) ethane

MFE: methyl nonafluorobuyl ether

Fluorinated Materials: Challenges

LHCE Challenges: HFE Mass/Weight



T. Waldmann, R.-G. Scurtu, K. Richter, and M. Wohlfahrt-Mehr, *J. Power Sources*, **472**, 228614 (2020).

The electrolyte amounts (1M $LiPF_6$ in EC:EMC = 3:7 (wt.%) + 2% VC) were 5 mL and 7 mL in the 18650 and 21700 cells, respectively.

SelectiLyte LP57 electrolyte

LP572 electrolyte (+ 2% VC) ~1.30 g/cm^3

18650: 5 ml = **6.5 g (electrolyte)**

18650: 46-47 g (total)

Panasonic/Sanyo NRC18650GA cell
3.50 Ah and 47.4 g
266 Wh/kg

X. Cao, L. Zou, B. E. Matthews, L. Zhang, X. He, X. Ren, M. H. Engelhard, S. D. Burton, P. Z. El-Khoury, H.-S. Lim, C. Niu, H. Lee, C. Wang, B. W. Arey, C. Wang, J. Xiao, J. Liu, W. Xu, and J.-G. Zhang, *Energy Storage Mater.*, **34**, 76 (2021).

LiFSI-1.2DME-2TFEO (mol ratio)

LiFSI (187.07): 1.0 mol = 187.07 g
DME (90.12): 1.2 mol = 108.14 g
TFEO (310.11): 2.0 mol = 620.22 g

4M DME-LiFSI (1.4-1.0 mol-mol) 1.33 g/cm^3 (MD simulation)
TFEO 1.46 g/cm^3 (expt)

about 2/1 TFEO/DME-LiFSI
(by volume)

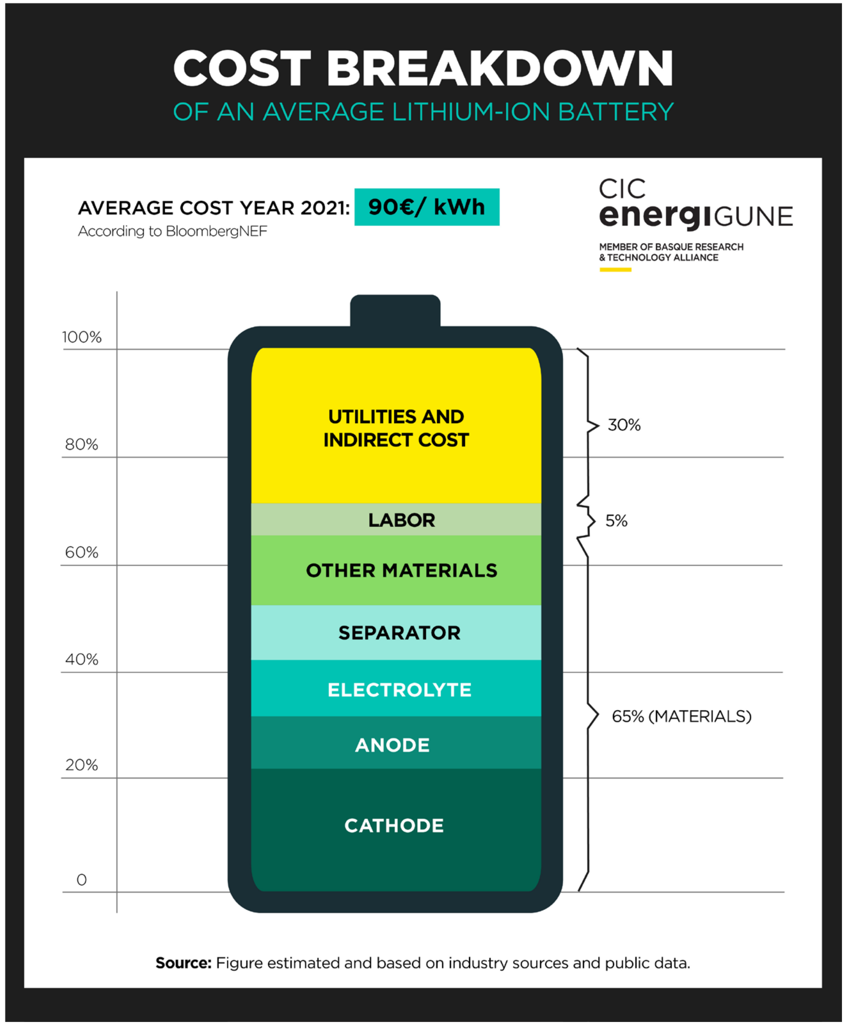
18650: 5 ml = **7.1 g (electrolyte)**

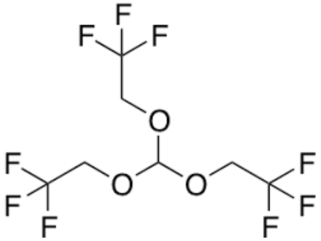
262 Wh/kg

(minor impact)

https://cicenergigune.com/en/blog/critical-materials-battery-industry

LHCE Challenges: HFE Cost

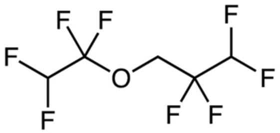




TFEO

97% 25 g $1195
http://synquestlabs.com/product/id/21402.html

95% 25 g $1844
https://www.sigmaaldrich.com/US/en/product/astatechinc/ate517251825?context=bbe

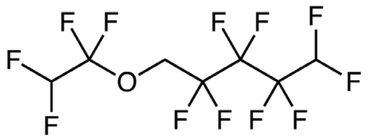


TTE

99% 25 g $95
http://www.synquestlabs.com/product/id/22001.html

>95% 25 g $54
https://www.tcichemicals.com/US/en/p/T3069

98% 25 g $25
https://www.oakwoodchemical.com/ProductsList.aspx?CategoryID=-2&txtSearch=6473&ExtHyperLink=1



OFE

>98% 25 g $159
https://www.tcichemicals.com/US/en/p/O0422

97% 25 g $50
http://www.synquestlabs.com/product/id/2151.html

98+% 25 g $181
https://www.fishersci.com/shop/products/1h-1h-5h-octafluoropentyl-1-1-2-2-tetrafluoroethyl-ether-tci-america-2/O042225G

18650: 5 ml = 7.1 g (electrolyte)
about 2/1 TFEO/DME-LiFSI
(by both volume… and mass)

~4.7 g of HFE (hydrofluoroether)

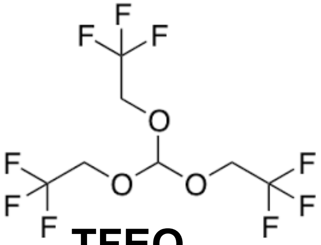
TFEO: $225 (for 25 g at $1195)
OFE: $30 (for 25 g at $159)

…**but COTS 18650 cells cost ~$3.50-4.25**
(when bought in 1000+ quantities)

(potentially high impact)

https://cicenergigune.com/en/blog/critical-materials-battery-industry

LHCE Challenges: HFE Flammability/Toxicity



TFEO

2. Hazard Identification

1) GHS pictogram

2) GHS signal word Warning

3) GHS hazard statement(s)

H302	Harmful if swallowed
H315	Causes skin irritation
H319	Causes serious eye irritation
H335	May cause respiratory irritation

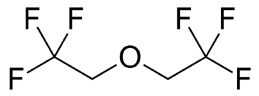
11. Toxicological Information

Acute toxicity:	No data available
Skin corrosion/irritation:	No data available
Serious eye damage/eye irritation:	No data available
Respiratory or skin sensitization:	No data available
Germ cell mutagenicity:	No data available
Carcinogenicity	
IARC:	No data available
ACGIH:	No data available
NTP:	No data available
OSHA:	No data available
Reproductive toxicity:	No data available
Routes of Exposure:	Inhalation, Eye contact, Ingestion, Skin contact
Specific target organ toxicity:	No data available
Aspiration hazard:	No data available

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

https://www.sigmaaldrich.com/US/en/product/astatechinc/ate517251825?context=bbe

LHCE Challenges: HFE Flammability/Toxicity



BTFE

bp: 61-62°C
fp: 1°C

2.1 Classification of the substance or mixture

GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)

Flammable liquids (Category 2), H225
Skin irritation (Category 2), H315
Eye irritation (Category 2A), H319
Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2 GHS Label elements, including precautionary statements

Pictogram 

Signal word Danger

Hazard statement(s)

H225	Highly flammable liquid and vapour.
H315	Causes skin irritation.
H319	Causes serious eye irritation.
H335	May cause respiratory irritation.

11.1 Information on toxicological effects

Acute toxicity
No data available
Dermal: No data available
No data available

Skin corrosion/irritation
No data available

Serious eye damage/eye irritation
No data available

Respiratory or skin sensitisation
No data available

Germ cell mutagenicity
No data available

Carcinogenicity

IARC:	No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.
NTP:	No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA:	No component of this product present at levels greater than or equal to 0.1% is on OSHA's list of regulated carcinogens.

Reproductive toxicity
No data available
No data available

Specific target organ toxicity - single exposure
Inhalation - May cause respiratory irritation.

Specific target organ toxicity - repeated exposure
No data available

Aspiration hazard
No data available

Additional Information
RTECS: KN3675000

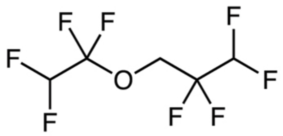
Convulsions, To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Stomach - Irregularities - Based on Human Evidence
Stomach - Irregularities - Based on Human Evidence

https://www.sigmaaldrich.com/US/en/sds/aldrich/287571

APPROVED FOR PUBLIC RELEASE

LHCE Challenges: HFE Flammability/Toxicity



TTE

bp: 93°C
fp: 27°C

2.1. Classification of the substance or mixture

Classification (GHS-US)

Flam. Liq. 3	H226 -	Flammable liquid and vapour
Skin Irrit. 2	H315 -	Causes skin irritation
Eye Irrit. 2A	H319 -	Causes serious eye irritation
STOT SE 3	H336 -	May cause drowsiness or dizziness
STOT SE 3	H335 -	May cause respiratory irritation

Full text of H-phrases: see section 16

2.2. Label elements

GHS-US labeling

Hazard pictograms (GHS-US) :

GHS02 GHS07

Signal word (GHS-US) : Warning

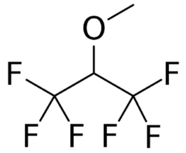
Hazard statements (GHS-US) : H226 - Flammable liquid and vapor
H315 - Causes skin irritation
H319 - Causes serious eye irritation
H335 - May cause respiratory irritation
H336 - May cause drowsiness or dizziness

11.1. Information on toxicological effects

Skin corrosion/irritation	: Causes skin irritation.
Serious eye damage/irritation	: Causes serious eye irritation.
Respiratory or skin sensitization	: Not classified
Germ cell mutagenicity	: Not classified
Carcinogenicity	: Not classified
Reproductive toxicity	: Not classified
Specific target organ toxicity (single exposure)	: May cause drowsiness or dizziness. May cause respiratory irritation.
Specific target organ toxicity (repeated exposure)	: Not classified
Aspiration hazard	: Not classified
Symptoms/injuries after inhalation	: May cause drowsiness or dizziness.

http://www.synquestlabs.com/msds/2100/2107-3-56.pdf

LHCE Challenges: HFE Flammability/Toxicity



HFME (or Isoflurothyl)
bp: 50^{o}C
fp: >93^{o}C

2. HAZARD(S) IDENTIFICATION

OSHA Haz Com: CFR 1910.1200: WHMIS 2015:	Not classifiable
Signal word:	None
Hazard Statement(s):	None
Pictogram(s) or Symbol(s):	None
Precautionary Statement(s):	None
Hazards not otherwise classified: [HNOC]	None.

11. TOXICOLOGICAL INFORMATION

RTECS Number: KO2282000

Acute Toxicity:
ipr-mus LD50:30 g/kg

Skin corrosion/irritation:
No data available

Serious eye damage/irritation:
No data available

Respiratory or skin sensitization:
No data available

Germ cell mutagenicity:
No data available

Carcinogenicity:
No data available

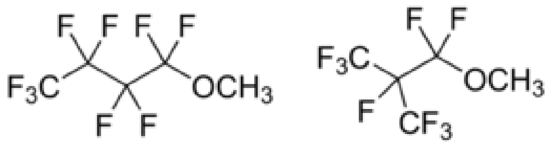
IARC: No data available **NTP:** No data available **OSHA:** No data available

Reproductive toxicity:
No data available

Target organ(s): No data available

https://en.wikipedia.org/wiki/Isoflurothyl
https://www.tcichemicals.com/US/en/p/H1524#docomentsSectionPDP

LHCE Challenges: HFE Flammability/Toxicity



MFE (mixture of isomers)
bp: 60°C
fp: NA

2. HAZARD(S) IDENTIFICATION

OSHA Haz Com: CFR 1910.1200: WHMIS 2015:	Not classifiable
Signal word:	None
Hazard Statement(s):	None
Pictogram(s) or Symbol(s):	None
Precautionary Statement(s):	None
Hazards not otherwise classified: [HNOC]	None.

11. TOXICOLOGICAL INFORMATION

Acute Toxicity:
No data available

Skin corrosion/irritation:
No data available

Serious eye damage/irritation:
No data available

Respiratory or skin sensitization:
No data available

Germ cell mutagenicity:
No data available

Carcinogenicity:
No data available

IARC: No data available **NTP:** No data available **OSHA:** No data available

Reproductive toxicity:
No data available

Target organ(s): No data available

(unknown impact)

9. PHYSICAL AND CHEMICAL PROPERTIES

Physical state (20°C):	Liquid
Form:	Clear
Colour:	Colorless - Almost colorless
Odour:	No data available
Odor threshold:	No data available
Odour threshold:	No data available

Melting point/freezing point:	No data available	pH:	No data available
Boiling point/range:	61°C	**Vapour pressure:**	No data available.
Decomposition temperature:	No data available	**Vapour density:**	No data available
Relative density:	1.53	**Dynamic Viscosity:**	No data available
Kinematic viscosity:	No data available		
Log Pow:	No data available	**Evaporation rate(Butyl Acetate=1):**	No data available
Flash point:	No data available	**Autoignition temperature:**	No data available
Flammability(solid, gas):	No data available	**Flammability or explosive limits:**	
		Lower:	No data available
		Upper:	No data available

Solubility(ies):

[Water]	No data available
[Other solvents]	No data available

https://www.tcichemicals.com/US/en/p/M1345#docomentsSectionPDP

LHCE Challenges: HFEs - Toxic Gases (HF)

SelectiLyte LP57 electrolyte

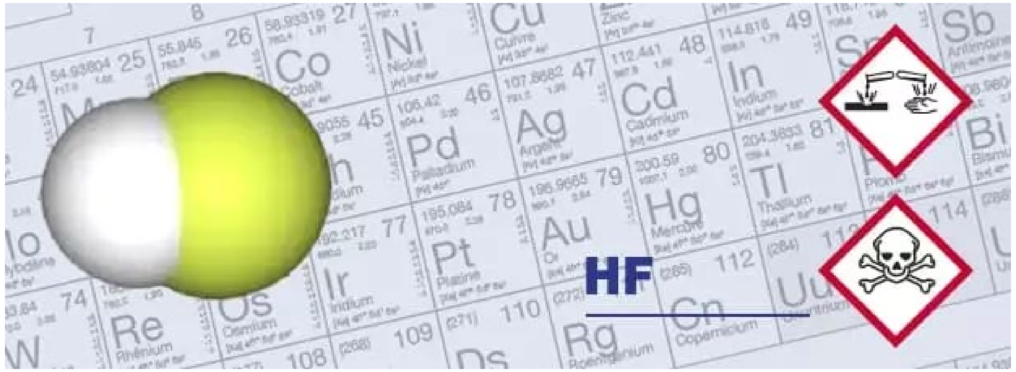
1M $LiPF_6$ in EC/EMC (3/7)

$$5 \text{ ml elect} \times \frac{1 \text{ L}}{1000 \text{ ml}} \times \frac{1 \text{ mol } LiPF_6}{\text{L elect}} = 0.005 \text{ mol } LiPF_6$$

= 0.03 mol F

= 0.03 mol HF

0.60 g HF = 0.52 L $HF_{(g)}$ produced from 1 single 18650 cell



1.15 g/L HF and 20.006 g/mol HF

LiFSI-1.2DME-2TFEO (mol ratio)

LiFSI (187.07): 1.0 mol = 187.07 g
DME (90.12): 1.2 mol = 108.14 g
TFEO (310.11): 2.0 mol = 620.22 g

915.43 g/mol elect

$$7.1 \text{ g} \times \frac{\text{mol elect}}{915.32 \text{ g}} = 0.00776 \text{ mol elect}$$

= 0.00776 mol LiFSI = 0.0155 mol HF

= 0.01551 mol TFEO = 0.1396 mol HF

= 0.155 mol HF (total)

> 5x as much HF produced

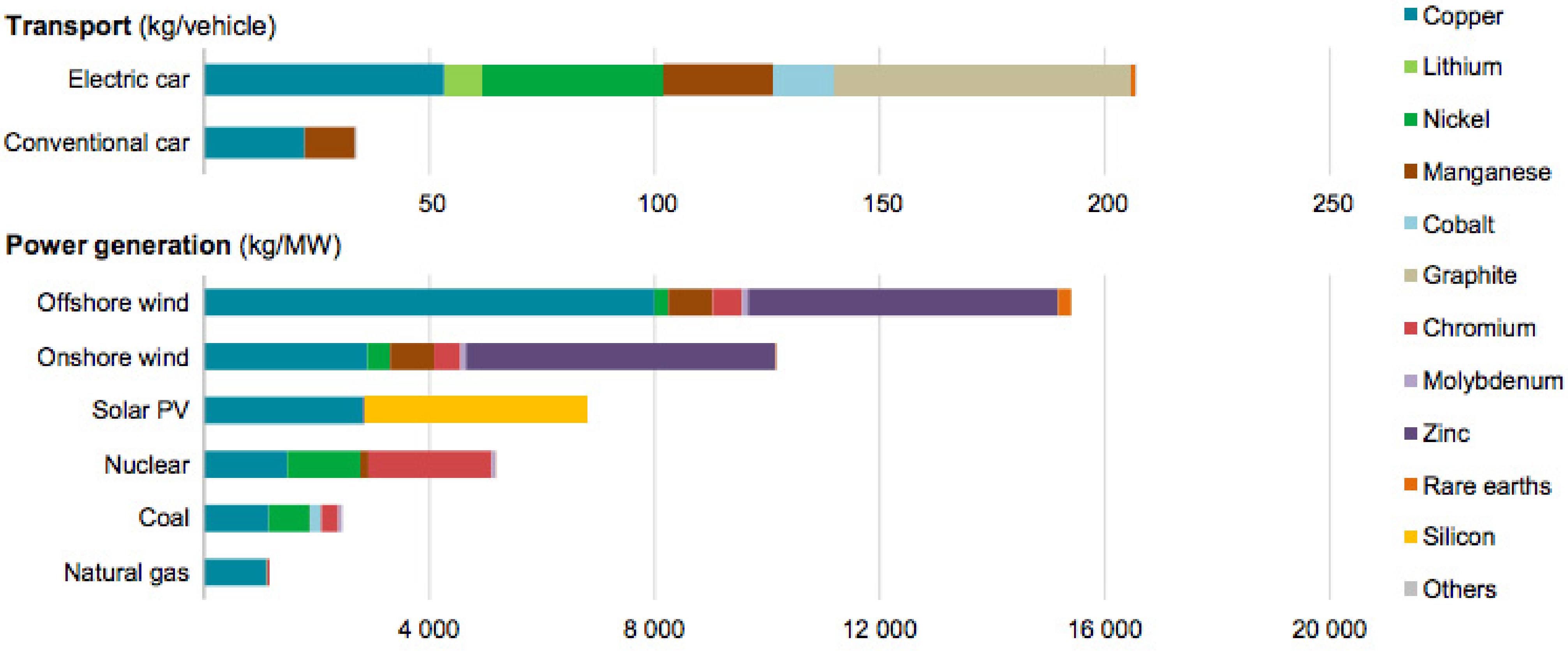
3.10 g HF = 2.70 L $HF_{(g)}$ produced from 1 single 18650 cell

(unknown impact)

A. Hammami, N. Raymond, and M. Armand, *Nature*, **424**, 635 (2003).
F. Larsson, P. Andersson, P. Blomqvist, and B.-E. Mellander, *Sci. Rep.*, **7**, 1 (2017).
Y. Peng, L. Yang*, X. Ju, B. Liao, K. Ye, L. Li, B. Cao, and Y. Ni, *J. Haz. Mater.*, **381**, 120916 (2020).

(* neglected: PVDF and any FEC in the cell)

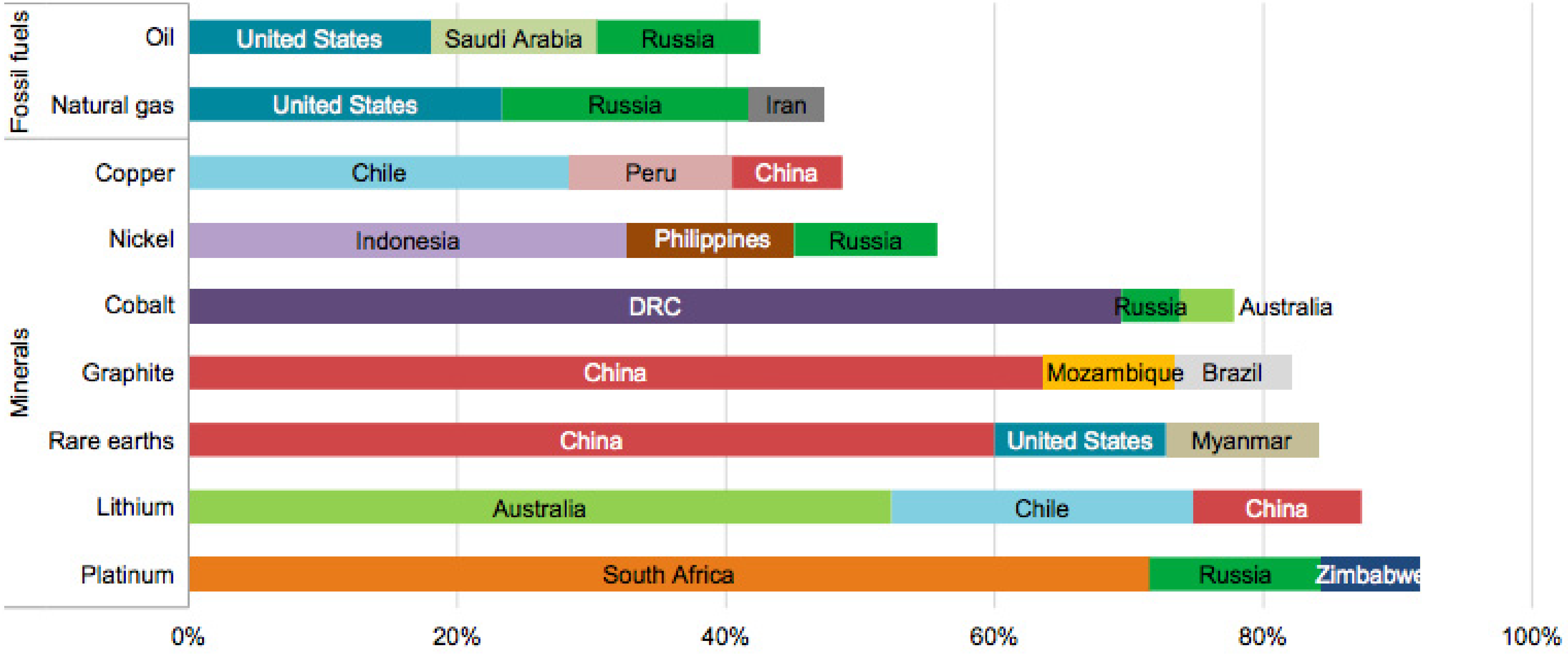
Food-For-Thought



Minerals used in selected clean energy technologies and fossil fuel technologies. Source: IEA

https://www.carbonbrief.org/iea-mineral-supplies-for-electric-cars-must-increase-30-fold-to-meet-climate-goals

Food-For-Thought



Share of top three producing countries in total production for selected minerals and fossil fuels, 2019. Source: IEA

https://www.carbonbrief.org/iea-mineral-supplies-for-electric-cars-must-increase-30-fold-to-meet-climate-goals

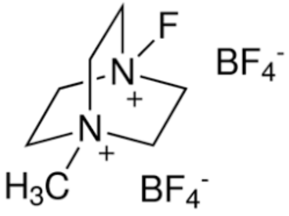
LHCE Challenges: Fluorine Availability

How are Fluorinated Solvents (i.e., Organofluorine Compounds) Produced?

…multiple synthesis routes for C-F bonds:

Direct Fluorination: $R_3CH + F_2 \rightarrow R_3CF + HF$

Electrophilic Fluorination: e.g., SelectFluor



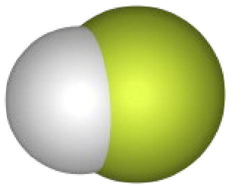
Electrosynthetic Methods: e.g., (molten) $K^+[F\text{-}H\text{-}F]^-$ $\quad 2\ HF + KOH \rightarrow KHF_2 + H_2O$

Nucleophilic Fluorination: $R_3CCl + MF \rightarrow R_3CF + MCl$ (M = Na, K, Cs)

Deoxofluorination: $RCO_2H + SF_4 \rightarrow RCF_3 + SO_2 + HF$

Elemental fluorine (F_2) and virtually all fluorine compounds are produced from **hydrogen fluoride** (**HF**) or its aqueous solutions, **hydrofluoric acid** (**HF$_{(aq)}$**).

How is HF Produced?



Hydrogen fluoride (HF) is typically produced by the endothermic reaction between sulfuric acid and pure grades of the mineral fluorite (CaF_2):

$$\mathbf{CaF_2} + H_2SO_4 \rightarrow \mathbf{2\ HF} + CaSO_4$$

About 20% of manufactured HF is a byproduct of fertilizer production, which generates hexafluorosilicic acid (H_2SiF_6). This acid can be degraded to release HF thermally and by hydrolysis:

$$\mathbf{H_2SiF_6} \rightarrow \mathbf{2\ HF} + SiF_4$$
$$SiF_4 + 2\ H_2O \rightarrow \mathbf{4\ HF} + SiO_2$$

https://en.wikipedia.org/wiki/Organofluorine_chemistry
https://en.wikipedia.org/wiki/Hydrogen_fluoride
https://en.wikipedia.org/wiki/Hexafluorosilicic_acid

LHCE Challenges: Fluorine Availability

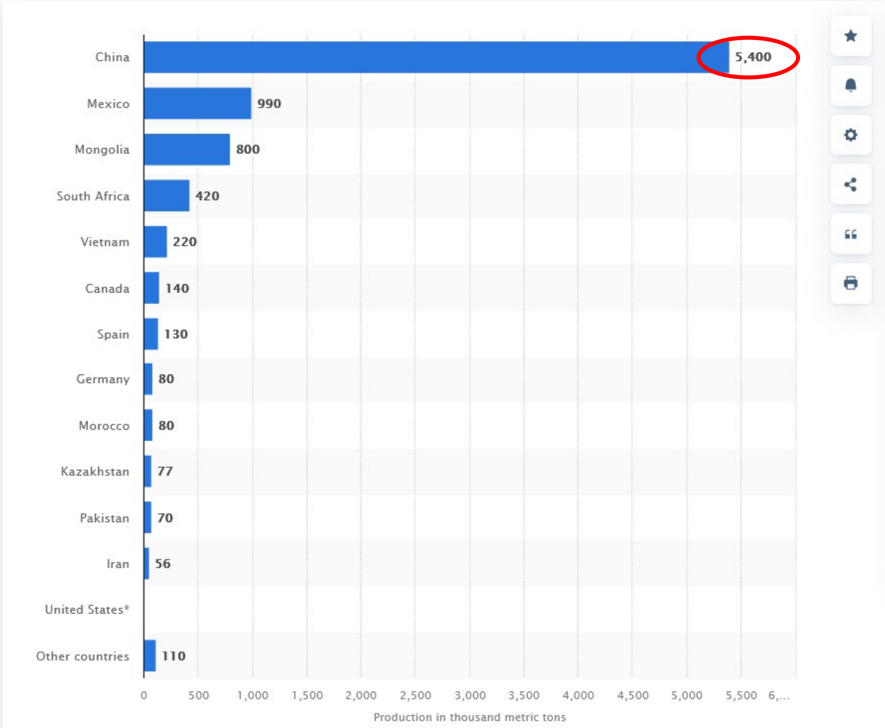
Fluorospar

Fluorite (CaF_2) is also called **fluorospar**

Chemicals & Resources › Mining, Metals & Minerals

Fluorspar mine production worldwide in 2021, by country

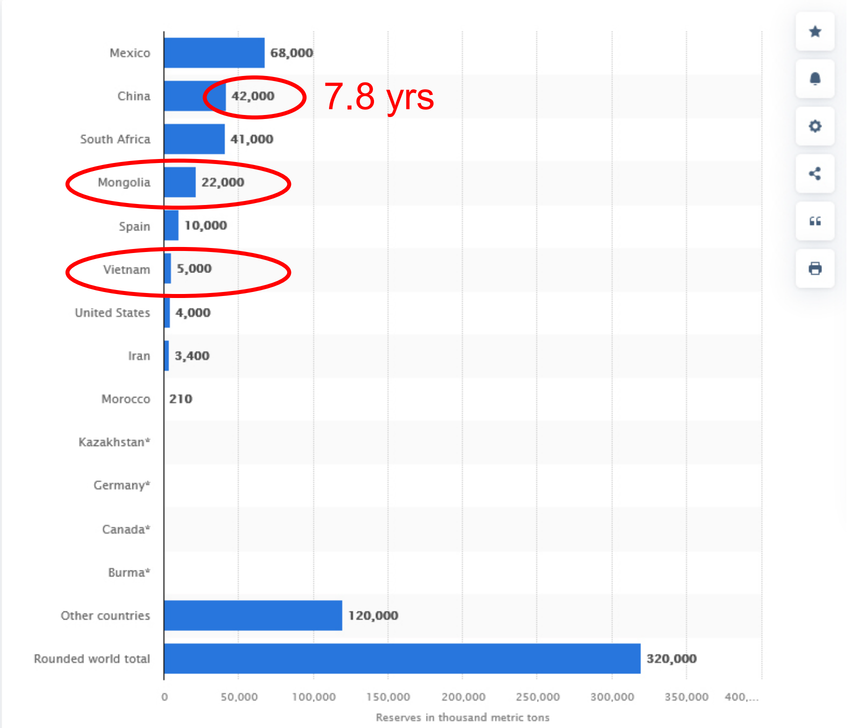
(in 1,000 metric tons)



Chemicals & Resources › Mining, Metals & Minerals

Fluorspar reserves worldwide in 2021 by country

(in 1,000 metric tons)



DEPARTMENT OF THE INTERIOR

Geological Survey

2022 Final List of Critical Minerals

AGENCY: U.S. Geological Survey, Department of the Interior.

ACTION: Notice.

SUMMARY: By this notice, the Secretary of the Interior, acting through the Director of the U.S. Geological Survey (USGS), presents the 2022 final list of critical minerals and the methodology used to develop the list. The 2022 final list of critical minerals, which revises the final list published by the Secretary in 2018, includes the following 50 minerals: Aluminum, antimony, arsenic, barite, beryllium, bismuth, cerium, cesium, chromium, cobalt, dysprosium, erbium, europium, fluorspar, gadolinium, gallium, germanium, graphite, hafnium, holmium, indium, iridium, lanthanum, lithium, lutetium, magnesium, manganese, neodymium, nickel, niobium, palladium, platinum, praseodymium, rhodium, rubidium, ruthenium, samarium, scandium, tantalum, tellurium, terbium, thulium, tin, titanium, tungsten, vanadium, ytterbium, yttrium, zinc, and zirconium.

https://en.wikipedia.org/wiki/Fluorite

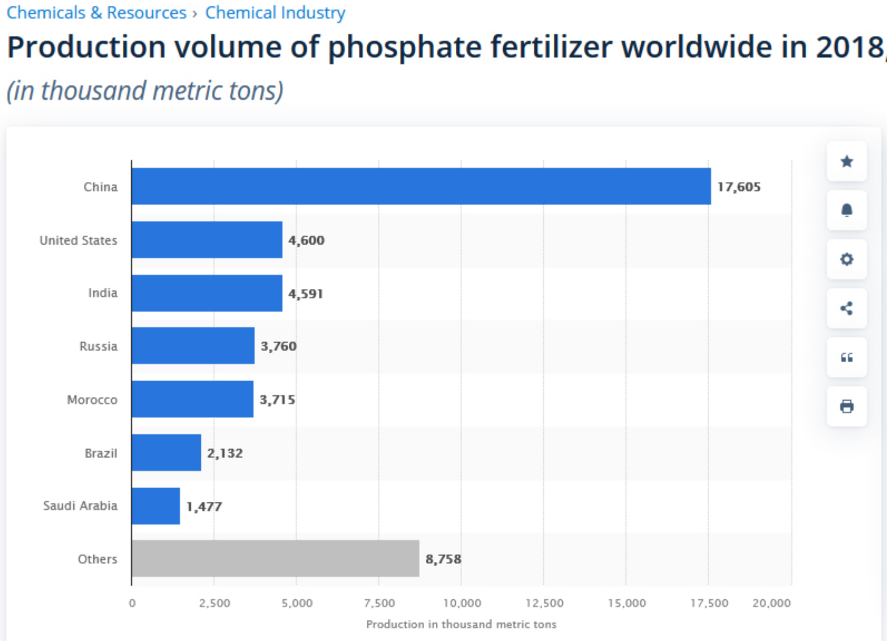
https://www.statista.com/statistics/1051717/global-fluorspar-production-by-country/

https://www.statista.com/statistics/270406/distribution-of-fluorspar-reserves-worldwide-by-country/

LHCE Challenges: Fluorine Availability

Fertilizer Production

Hexafluorosilicic acid (**H_2SiF_6**) is produced commercially from fluoride-containing minerals that also contain silicates. Specifically, apatite and fluorapatite minerals are treated with sulfuric acid to give phosphoric acid, a precursor to fertilizers. The method is called the **wet production process**.



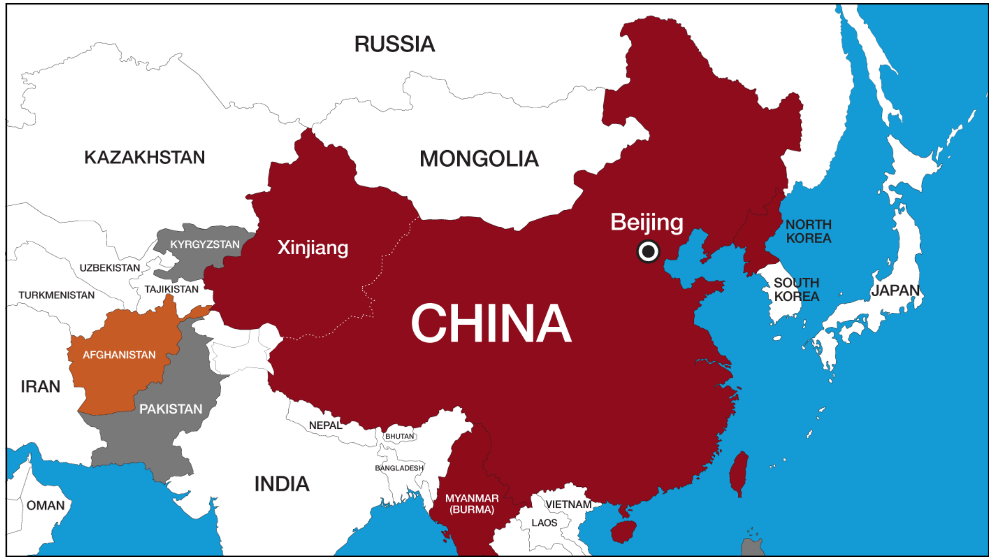
https://en.wikipedia.org/wiki/Hexafluorosilicic_acid

https://en.wikipedia.org/wiki/Phosphoric_acid

https://www.statista.com/statistics/1252657/phosphate-fertilizer-production-by-country/

Takeaways…

- Localized High Concentration Electrolytes (**LHCEs**) with **hydrofluoroethers** (**HFEs**) and related non-solvents are **critical enablers** for most **advanced battery chemistries** (i.e., Beyond Li-ion Batteries)
- **LHCEs** are THE **next class of advanced electrolytes** (with few other promising alternatives)



- The **high mass** of the **HFEs** does not seem to be problematic for cell energy density (minor impact)
- The **high cost** of the **HFEs** is a much greater concern in terms of substantially increasing cell costs (potentially high impact)
- The **flammability** of the **HFEs** is confusing – conflicting information (unknown impact)
- The **toxicity** of the **HFEs** is largely unexplored (unknown impact)
- **HF production** from the **HFEs may be a HUGE problem** (if the batteries burn)… or a non-problem (if the batteries do not burn) (unknown impact)
- **HFE production requires HF** – **China dominates** current world production of HF (as well as organofluorine chemical production such as HFEs) (critical resource concern – raw materials (fluorospar/fertilizers) and processed materials (HFEs))

That's all… Talk amongst yourselves… (questions?)

G. Nagasubramanian and K. Fenton, *Electrochim. Acta*, **101**, 3 (2013).