FB04 - Produktionstechnik
FG31 - Energiespeicher- und Energiewandlersysteme

Advances in electrochemical ion pumping for lithium recovery

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Conventional lithium recovery

- Pump water to pons
- Evaporate water for 12-18 months
- Separation of lower soluble salts from LiCl
- Precipitation of $Mg(OH)_2$ by using lime
- Precipitation of Li_2CO_3 by adding Na_2CO_3

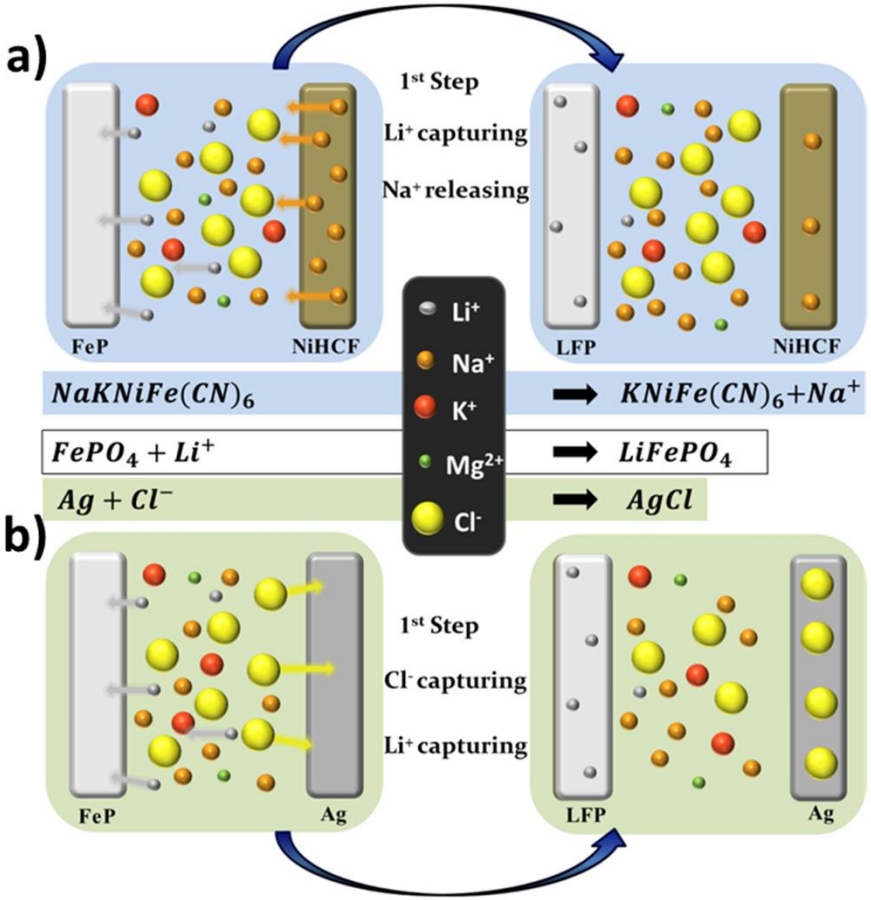
Non-conventional lithium sources

- Geological basins
- Hydrothermal sources
- Brackish water
- Oil&gas production sites
- Geothermal plants

360 t_{Li} y^{-1}

Challenge: capture the lithium while water flows

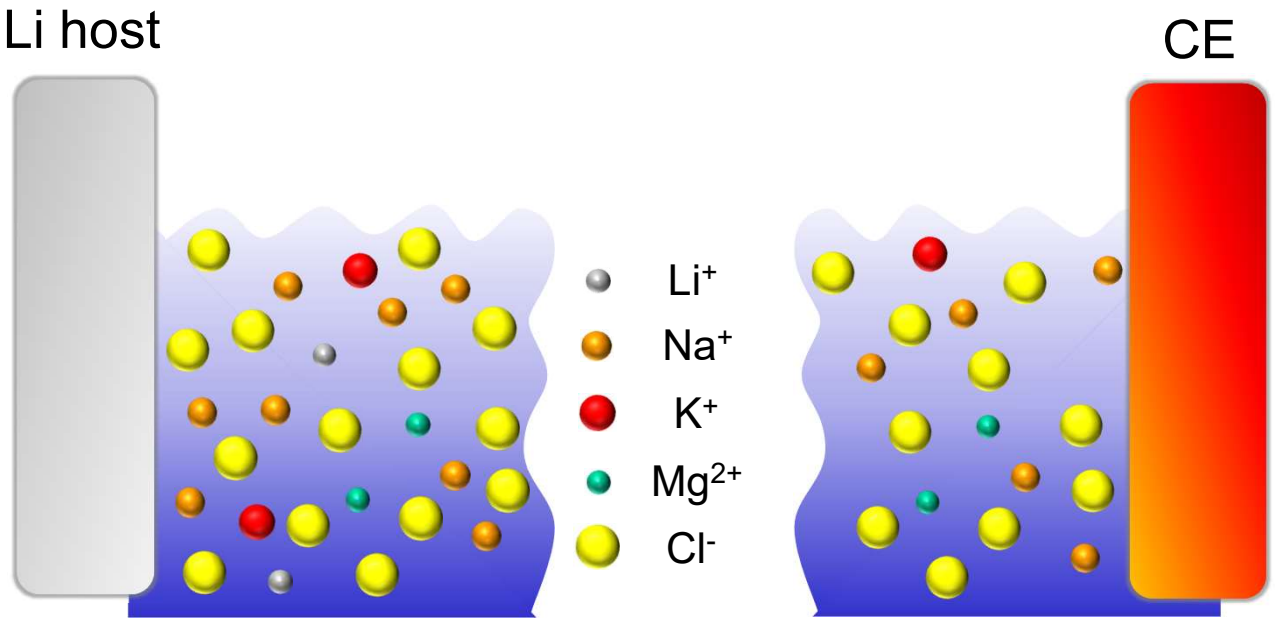
Lithium recovery by electrochemistry: the electrochemical ion pumping



Selective exchange

Salt capturing

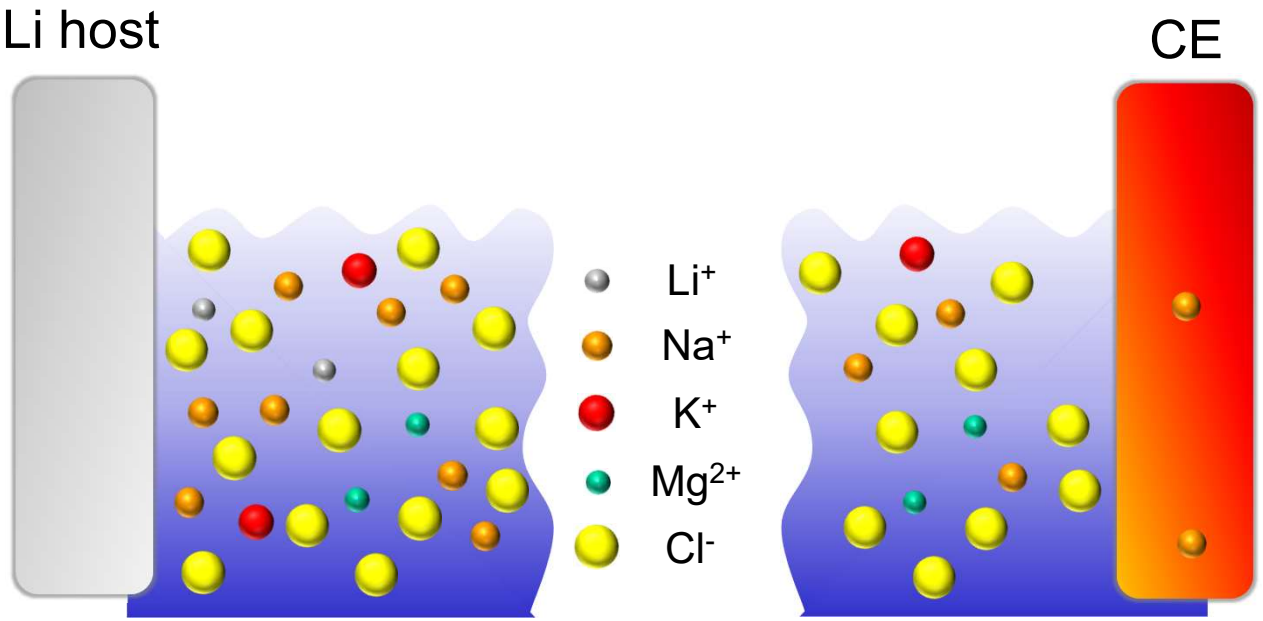
Lithium recovery by electrochemistry: the electrochemical ion pumping



Salt capturing

M. Pasta, et al., *Energy Environ. Sci.* 5 (2012) 9487

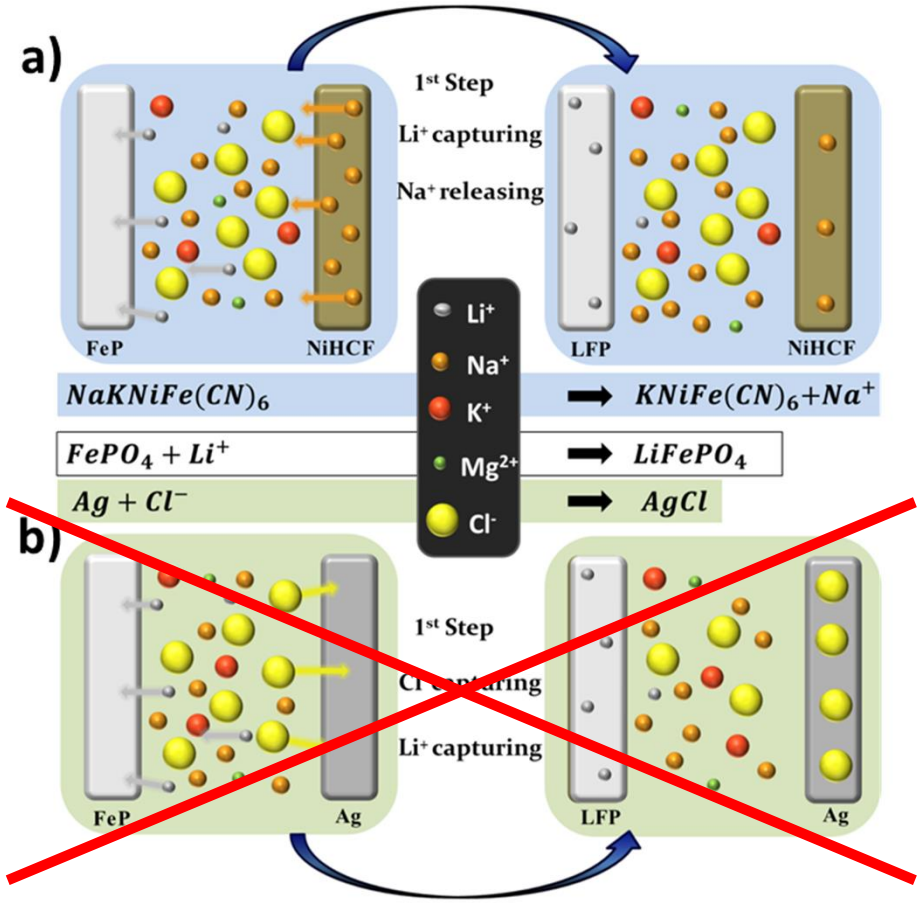
Lithium recovery by electrochemistry: the electrochemical ion pumping



Selective exchange

R. Trocoli, et al., ChemSusChem. 8 (2015) 2514

Comparing salt capturing and selective exchange: A simplified model



W_{SE} = 0.60 kWh kg^{-1}

NiHCF

W_{SC} = 0.30 kWh kg^{-1}

Silver

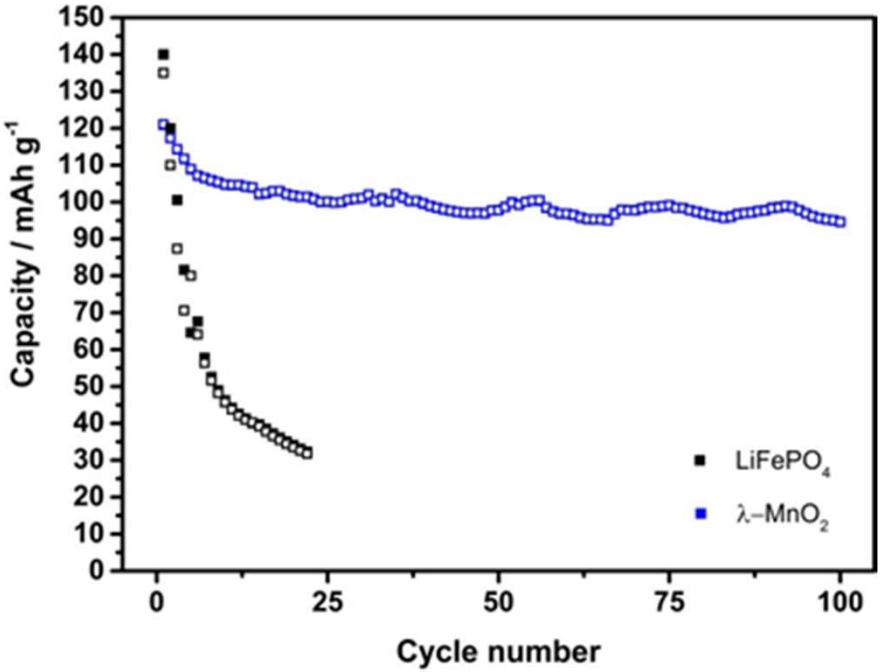
The lithium-selective material

$LiFePO_4$

	LiCl-NaCl	LiCl-KCl	$LiCl-MgCl_2$
Li (mM)	108±10	124±27	73±4
M (mM)	0.48±0.004	0.4±0.15	2.1±0.8
$K_{Li/M}$	245	310	34

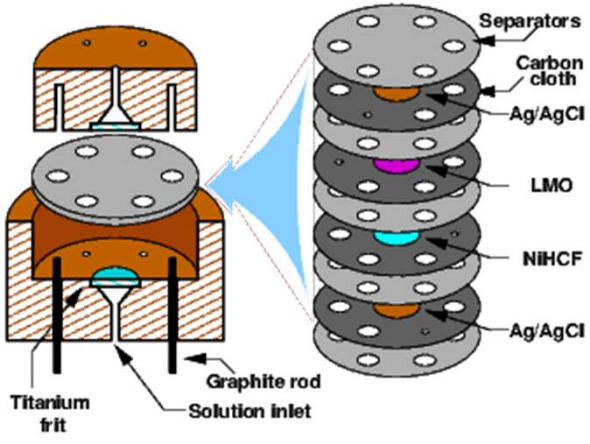
$LiMn_2O_4$

	LiCl-NaCl	LiCl-KCl	$LiCl-MgCl_2$
Li (mM)	44 ± 1	42 ± 6	63 ± 5
M (mM)	1.2 ± 0.2	1.4± 0.5	0.2 ± 0.02
$K_{Li/M}$	36.6	30	315

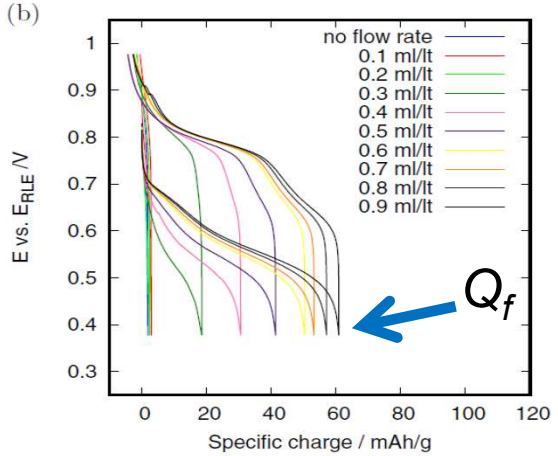


R. Trocoli, et al., *ChemElectroChem* 4 (2017) 143

The flow-through reactor



(b)



Molar flow

$$M_f = c_{Li} \cdot \Gamma$$

Relative Charge

$$\frac{Q_f}{Q_r}$$

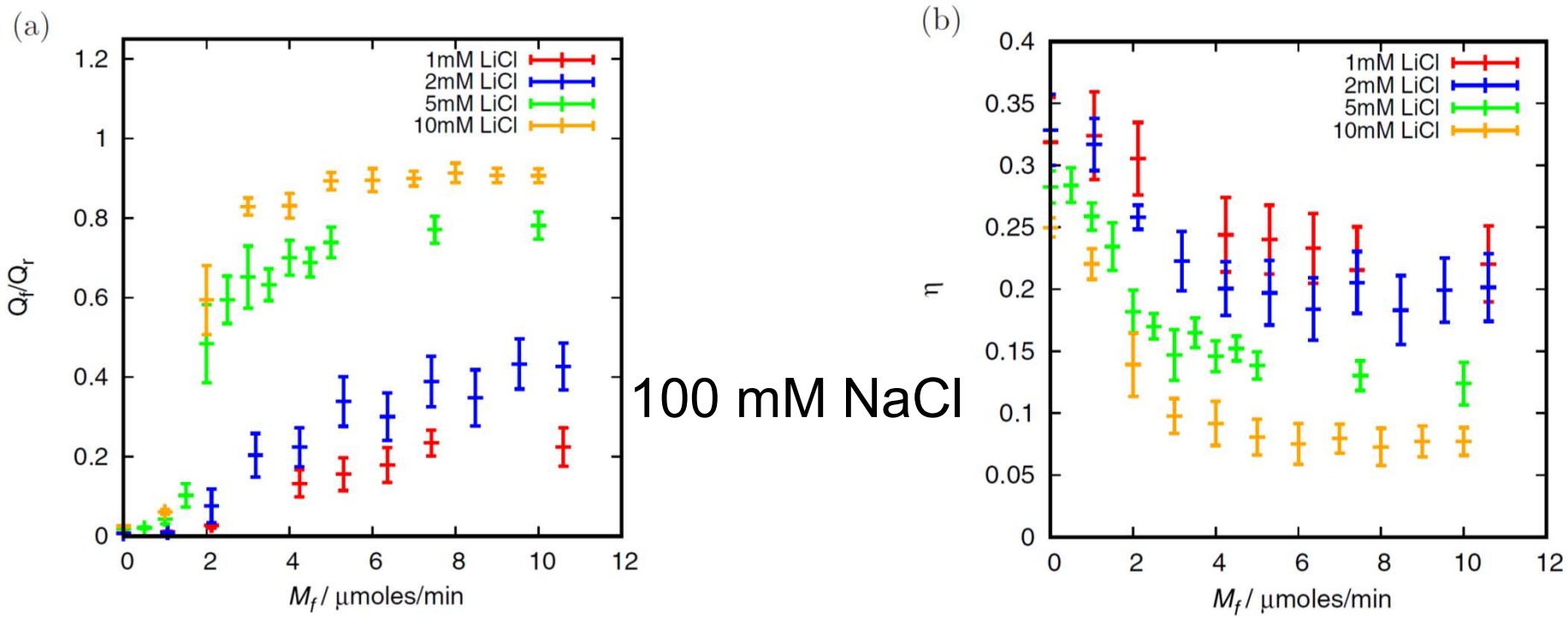
Average overpotential

$$\eta = \int_0^{Q_f} \left| E_{red}(Q) - E_{eq}(Q) \right| \cdot dQ$$

Sources with less than 50 ppm Li are strongly limited by diffusion in solution

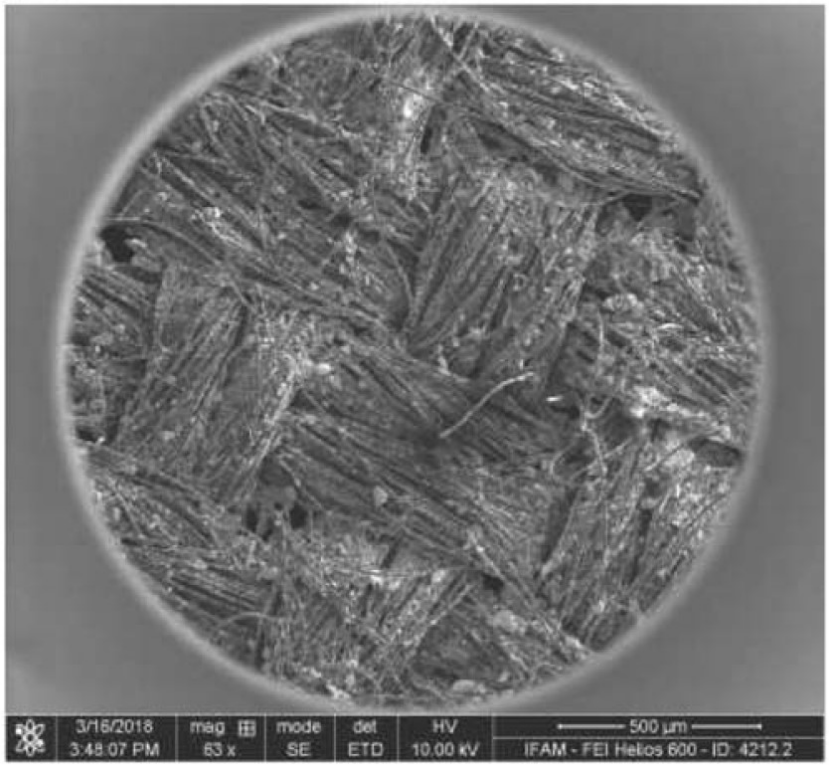
M.S. Palagonia, et al., *J. Electrochem. Soc.* 164 (2017) E586

Lithium capturing

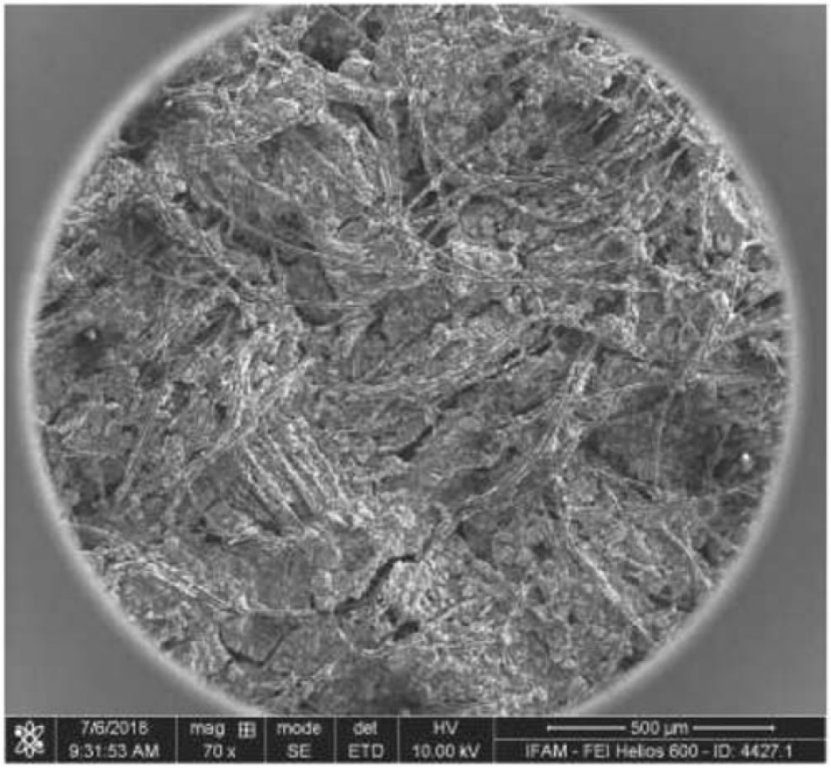


The limit performances are strongly dependent on the concentration of the source

Lithium capturing



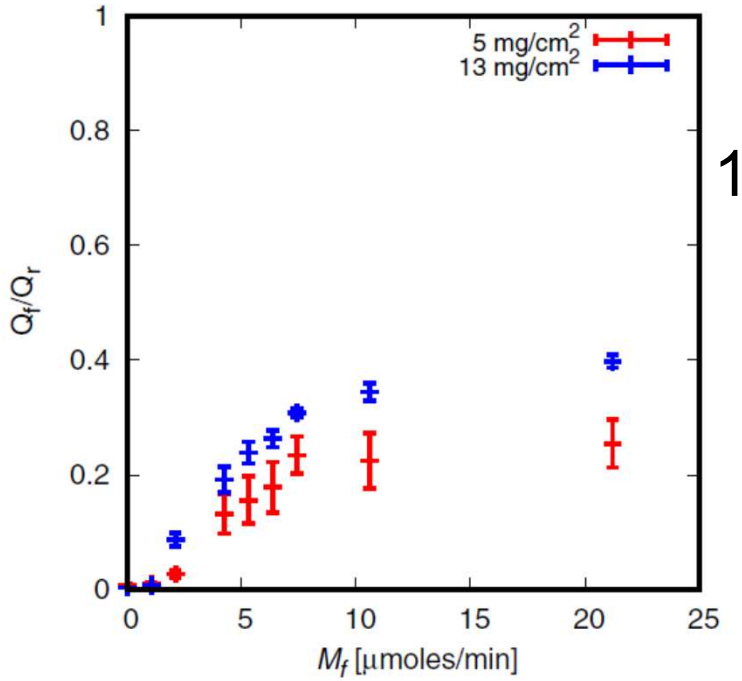
5 mg cm^{-2}



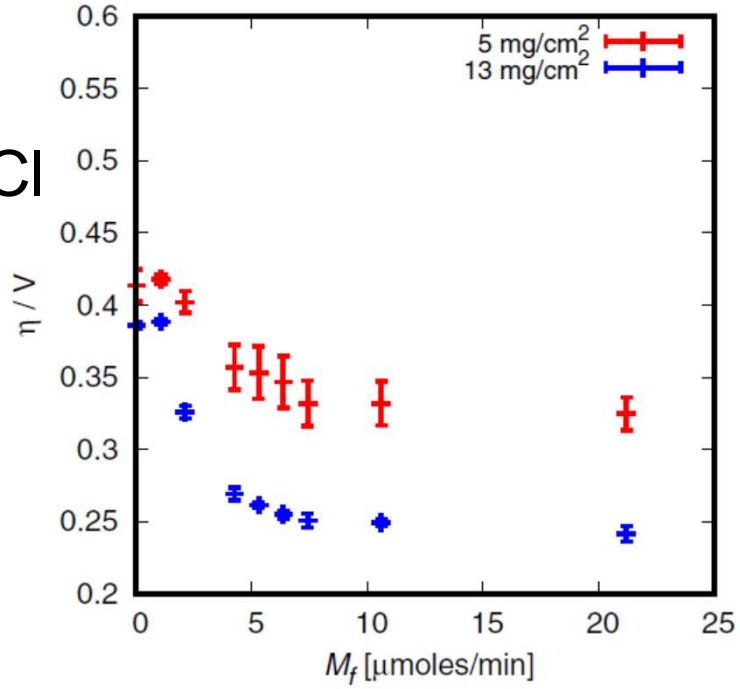
13 mg cm^{-2}

LMO badly dispersed on the carbon cloth

Lithium capturing



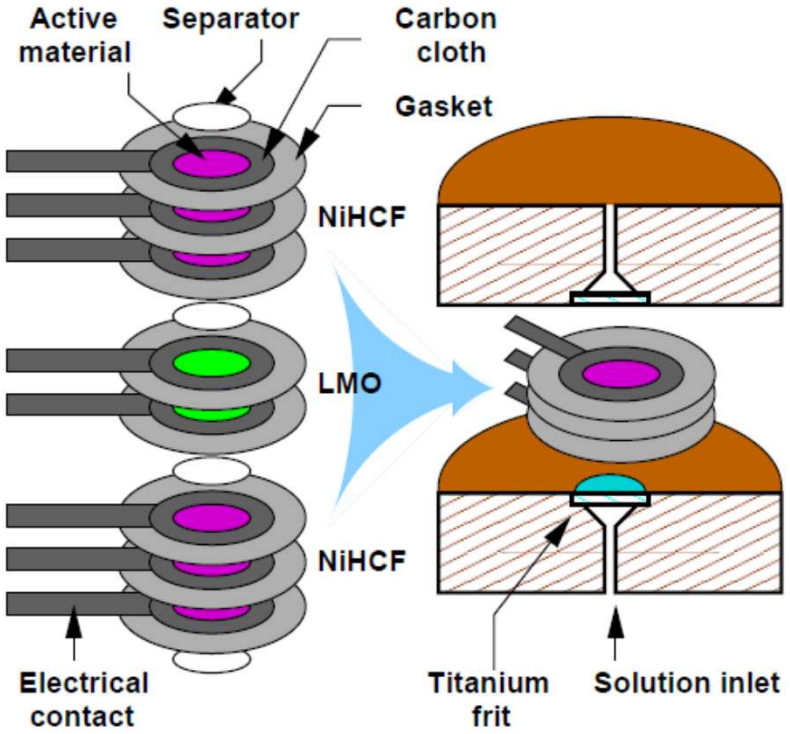
1 mM LiCl
100 mM NaCl



Higher mass loading helps capturing more lithium!

M.S. Palagonia, et al., J. Electrochem. Soc. 166 (2019) E286

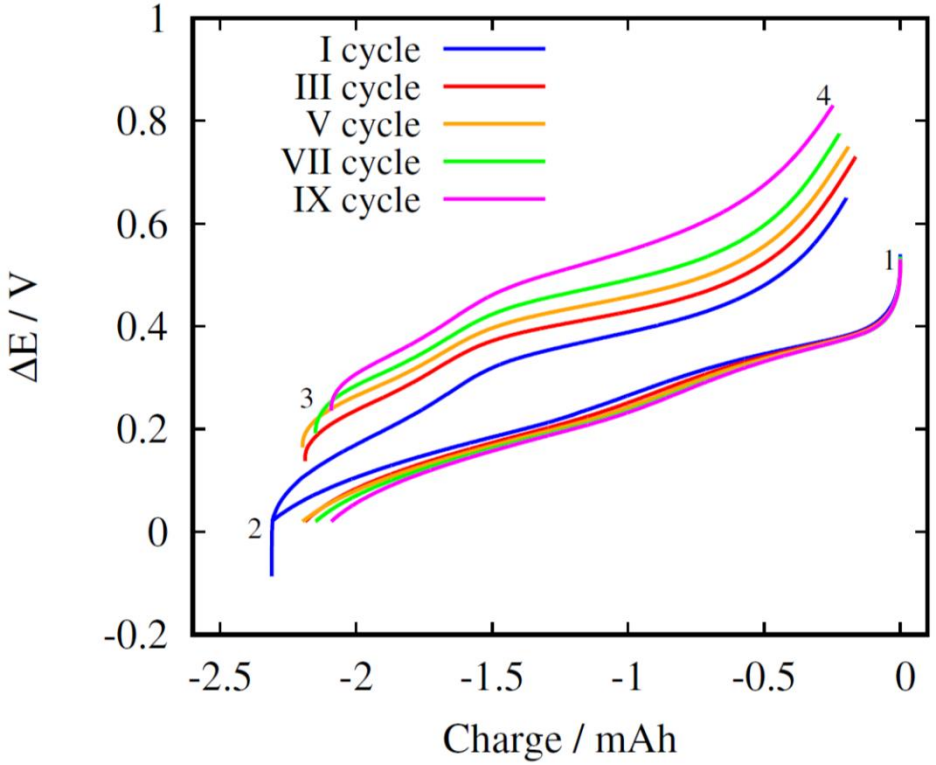
Full recovery cycle



1) Capturing from lithium source
2) Purging with air
3) Cleaning with rinsing solution
4) Purging with air
5) Releasing lithium in recovery solution

M.S. Palagonia, et al., Desalination 475 (2020) 114192

Full recovery cycle



9 recovery cycles

Li source: 1mM LiCl + 100 mM NaCl (150 mL each cycle)

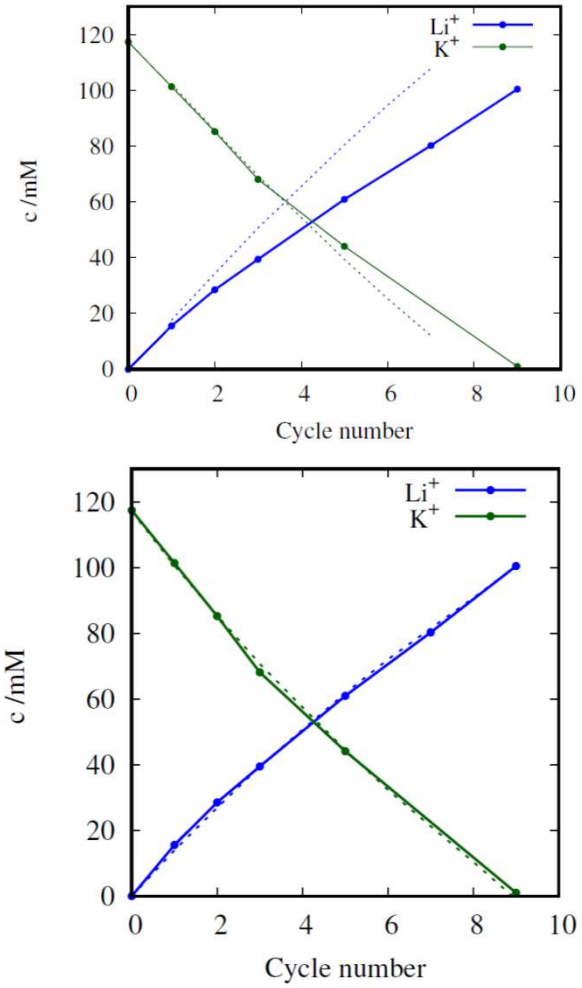
I_{red} = -500 µA cm^{-2}

Recovery: 120 mM KCl (5 mL)

I_{ox} = +1 mA cm^{-2}

M.S. Palagonia, et al., Desalination 475 (2020) 114192

Full recovery cycle

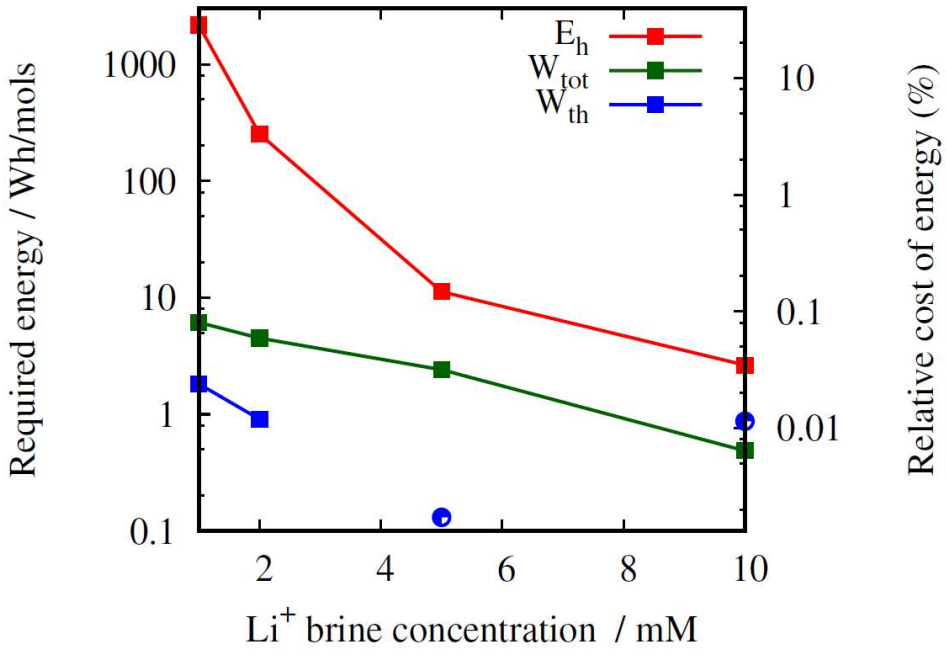


$$c_{Li,j} = \frac{c_{Li,j-1} \cdot V + |Q_j| / F}{V + V_d}$$

$$c_{K,j} = \frac{c_{K,j-1} \cdot V + c_{K,r} \cdot V_d - |Q_j| / F}{V + V_d}$$

V_d = 70 µL

$c_{Li,max}$ ≈ 750 mM



Summary

- There are many lithium sources (also in Europe) which cannot be exploited the nowadays lithium extraction process (lime-soda evaporation)
- Selective capturing of lithium ions from solution can be achieved with proper intercalation materials
- Mass transport of the lithium in solution is limiting in diluted solution (< 10 mM Li)
- It is economically feasible to recover lithium from solutions with lithium content below 7 ppm

People 4 Production

Acknowledgements

http://www.esecs.uni-bremen.de

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Thank you for your attention!