

Li-S and Li-Air Systems: The Characterization Challenge

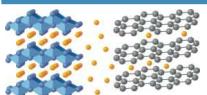
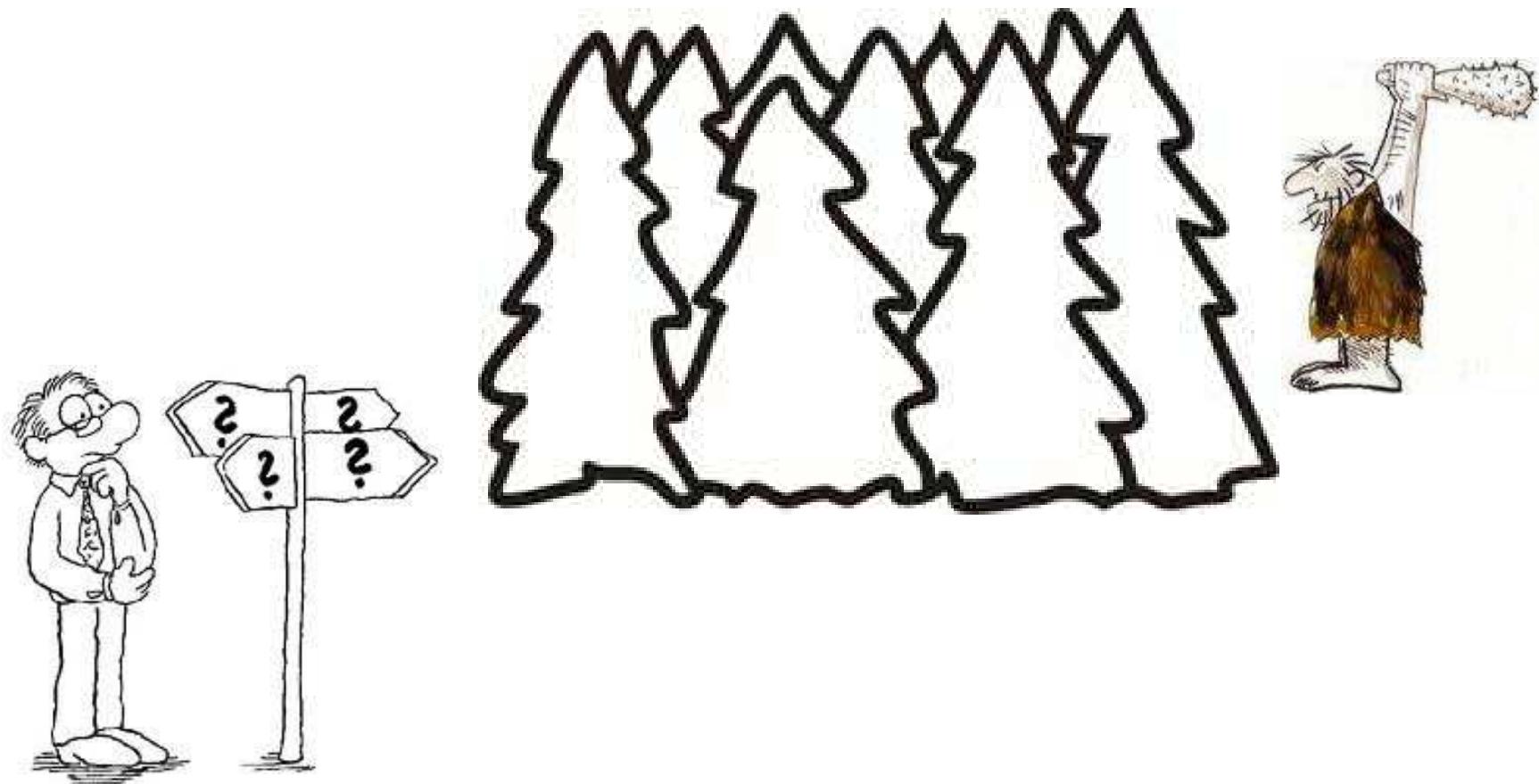


Petr Novák

**Anna Evans
Arnd Garsuch (BASF SE)
Hermann Kaiser
Pascal Maire
Tiphaine Poux
Holger Schneider**



Go beyond Li-ion! But what is there???



Go beyond Li-ion! But what is there???

MCl ₂ -Na NaAlCl ₄ -Al ₂ O ₃ *	TiS ₂ -Li LiAsF ₆	V ₂ O ₅ -Li LiAsF ₆	FeS ₂ -Li Org.	CoO ₂ -Li LiAsF ₆ /LiBF ₄
CF ₃ -Li LiBF ₄	SO ₂ -Li LiBr	SOCl ₂ -Li LiAlCl ₄	I ₂ P2VP-Li LiI	CuO-Li LiClO ₄
Br ₂ -Zn ZnBr ₂	MnO ₂ -Li LiClO ₄	NiOOH-MH KOH	O ₂ -H ₂ POLYMER	MnO ₂ -H ₂ KOH
Na-S β-Al ₂ O ₃ *	FeS ₂ -LiAl LiCl.KCl*	NiOOH-H ₂ KOH	O ₂ -Al KOH/NaOH	
MnO ₂ -Al AlCl ₃	O ₂ -H ₂ H ₃ PO ₄	CuCl-Mg NaCl	CaCrO ₄ -Ca LiCl.KCl*	O ₂ -Zn KOH
O ₂ -H ₂ Li ₂ CO ₃ /K ₂ CO ₃ *	AgCl-Mg NaCl	MnO ₂ -Zn KOH	O ₂ -H ₂ KOH	Ag ₂ O-Cd KOH
PbO ₂ -Sb H ₂ SO ₄	MnO ₂ -Mg Mg(ClO ₄) ₂	NiOOH-Zn KOH	Ag ₂ O-Zn KOH	HgO-Cd KOH
PbO ₂ -Pb HClO ₄ -HBF ₄	PbO ₂ -Zn pH ₄	NiOOH-Cd KOH	HgO-Zn KOH	
PbO ₂ -Pb H ₂ SO ₄	MnO ₂ -Zn NH ₄ Cl-ZnCl ₂	NiOOH-Fe KOH	CuO-Zn KOH	

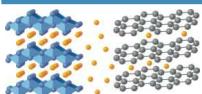


Faraday Law

$$Q = zF \frac{m}{M}$$

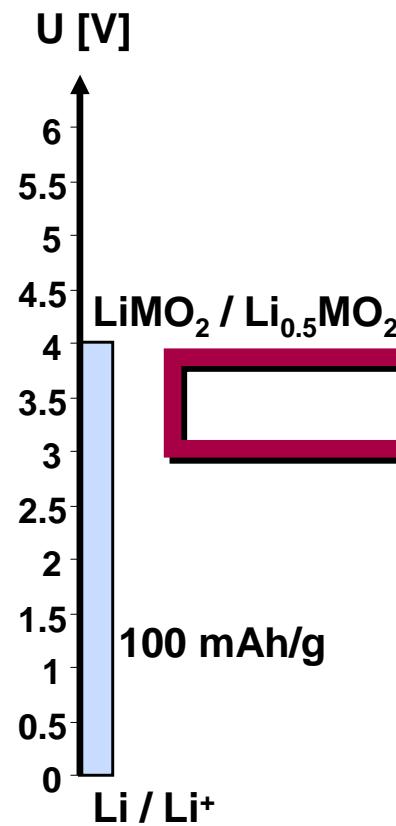
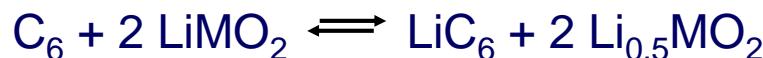
Specific Energy

$$W = U Q$$

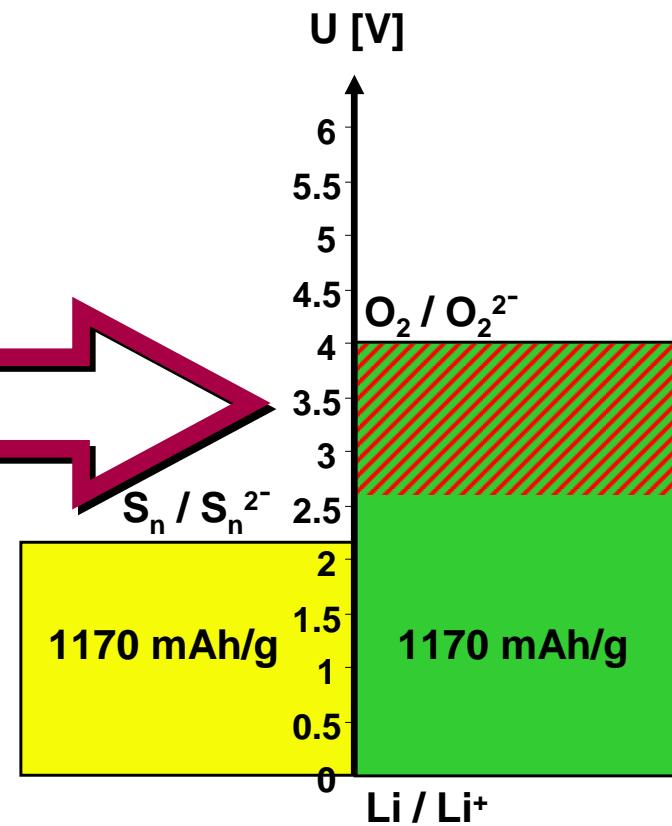
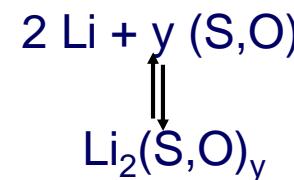


Battery Materials

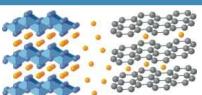
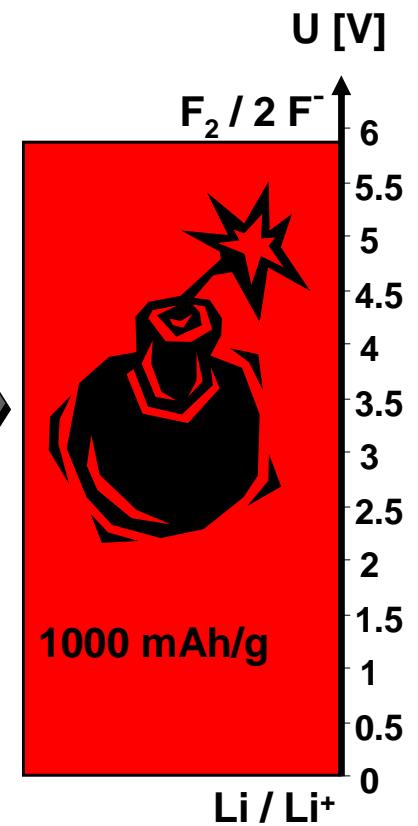
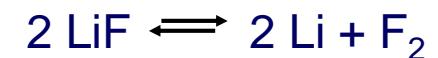
2nd/3rd Generation



4th Generation

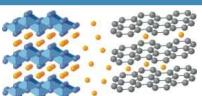


5th Generation ?

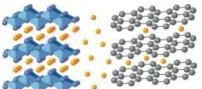
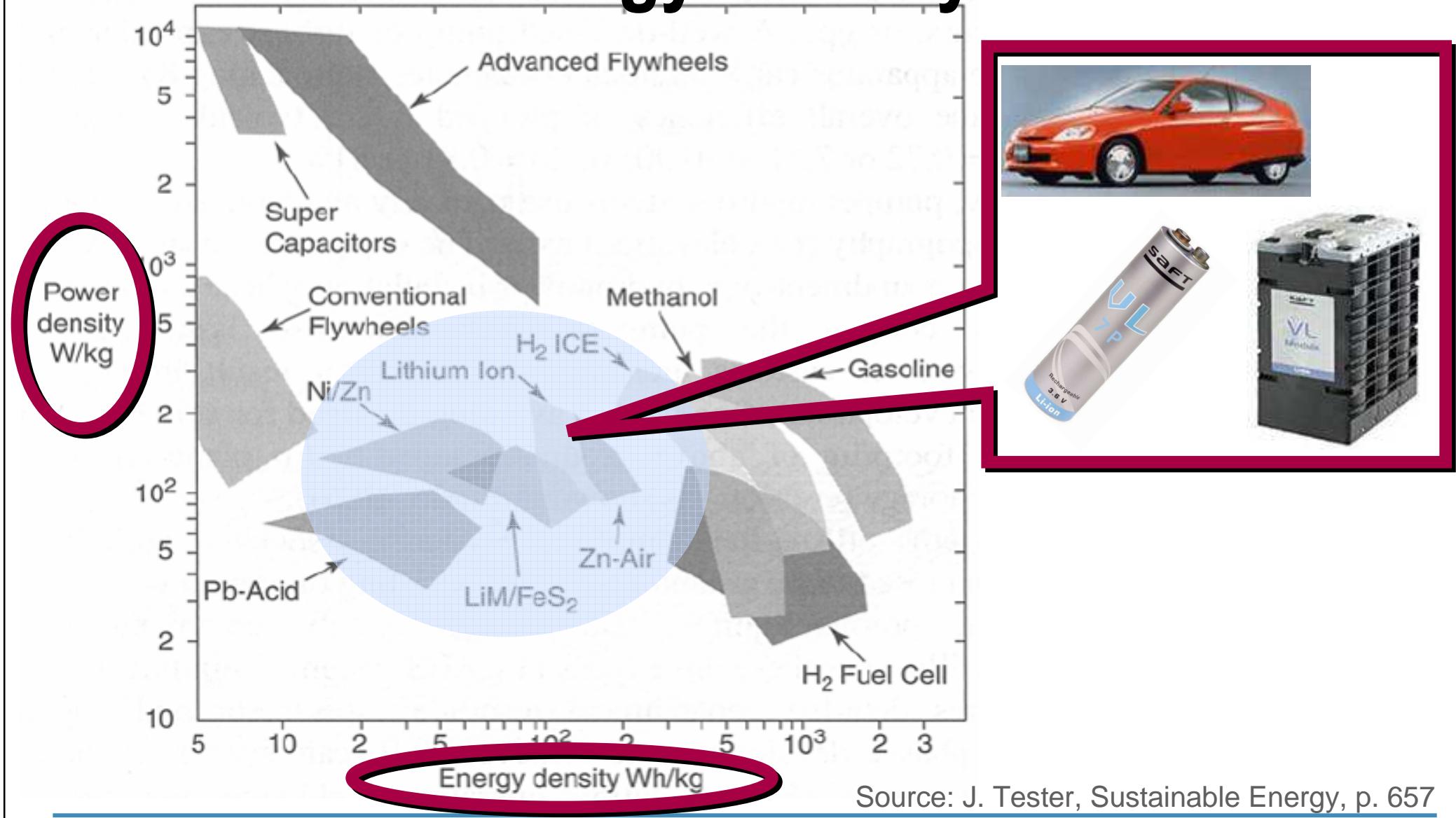


The Characterization Challenge (I)

The “simple” ELECTROCHEMISTRY



POWER vs. Energy Density



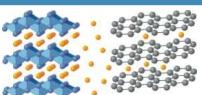
What do WE normally characterize?

- **Specific charge** of the material (mAh/g)
- **Voltage** of a half-cell (V vs. Li)
- And sometimes the **cycling** behavior...

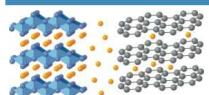
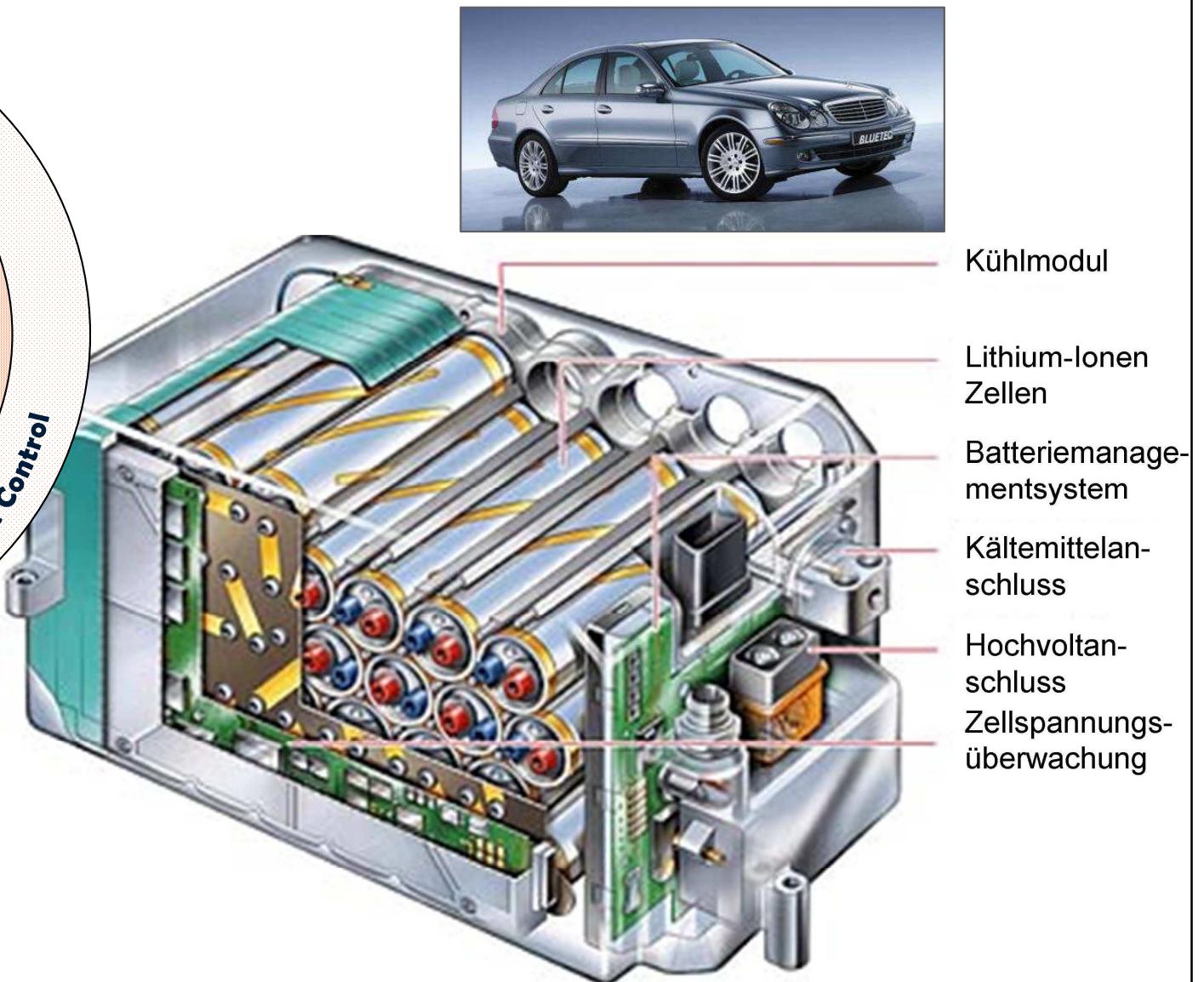
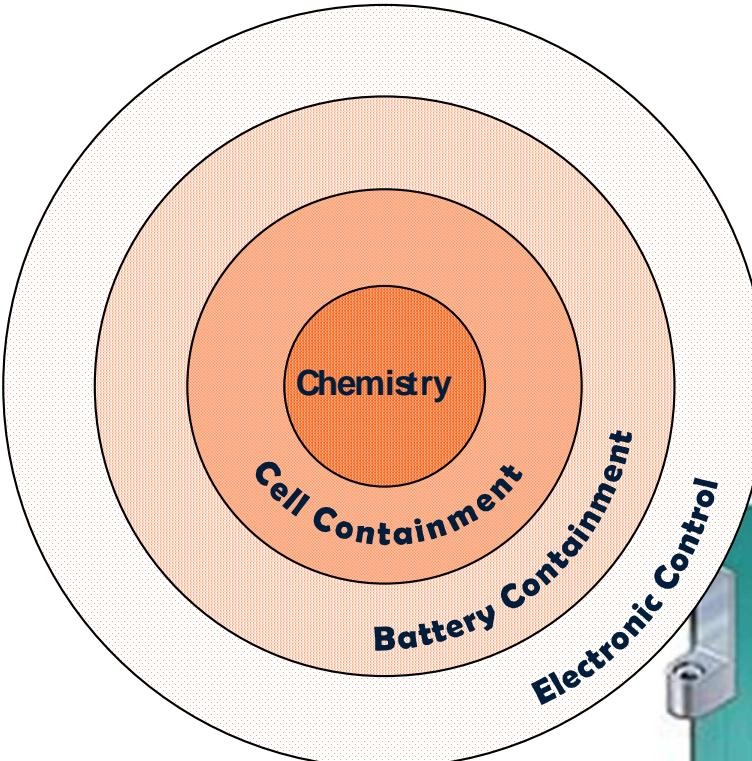


ca. 1800 mAh/g @ 4V

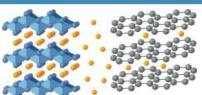
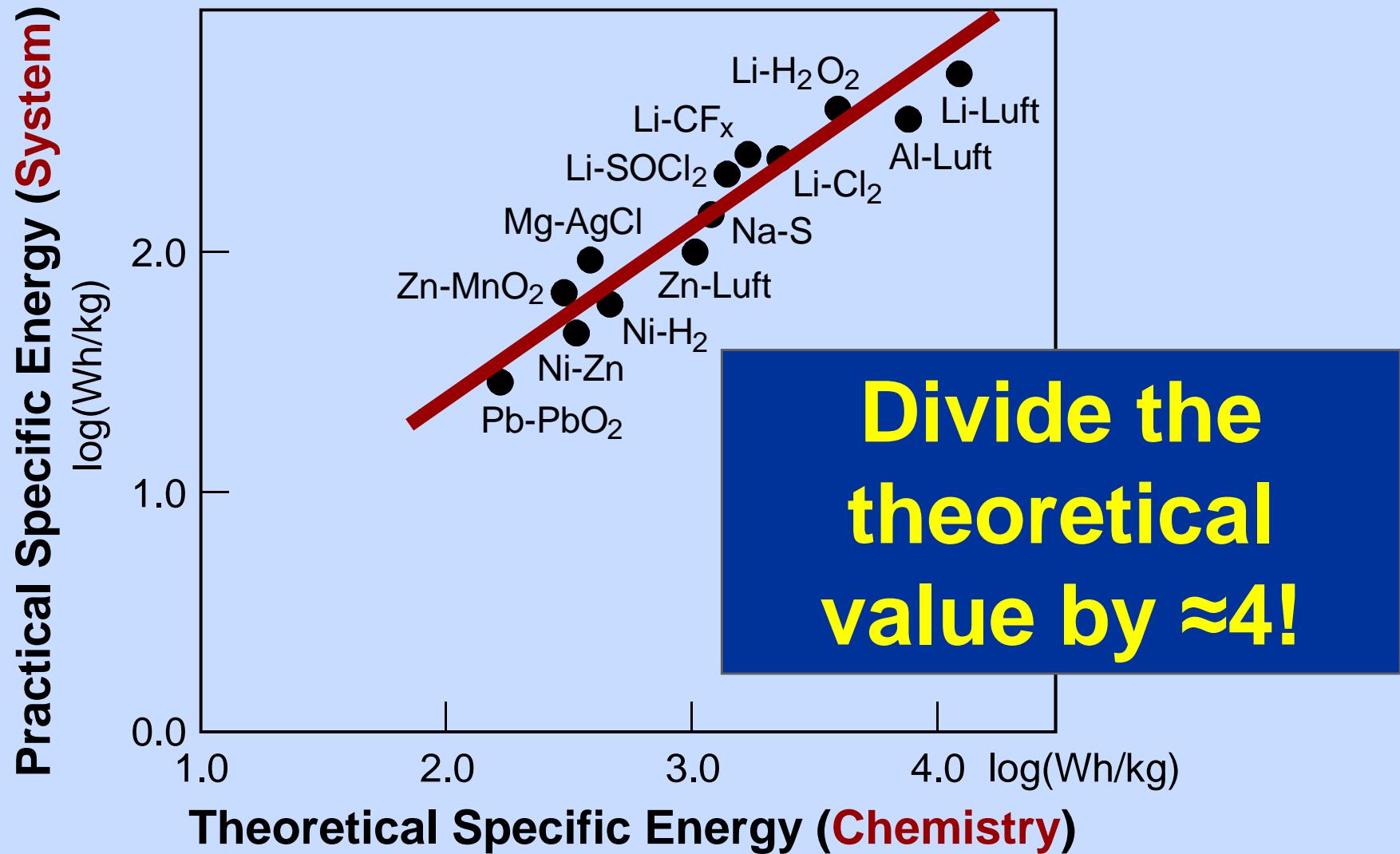
⇒ 7200 Wh/kg



What is a REAL Battery?



Specific Energy



Specific Energy

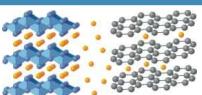


ca. 1800 mAh/g @ 4V

$\Rightarrow \underline{\text{7200 Wh/kg}}$

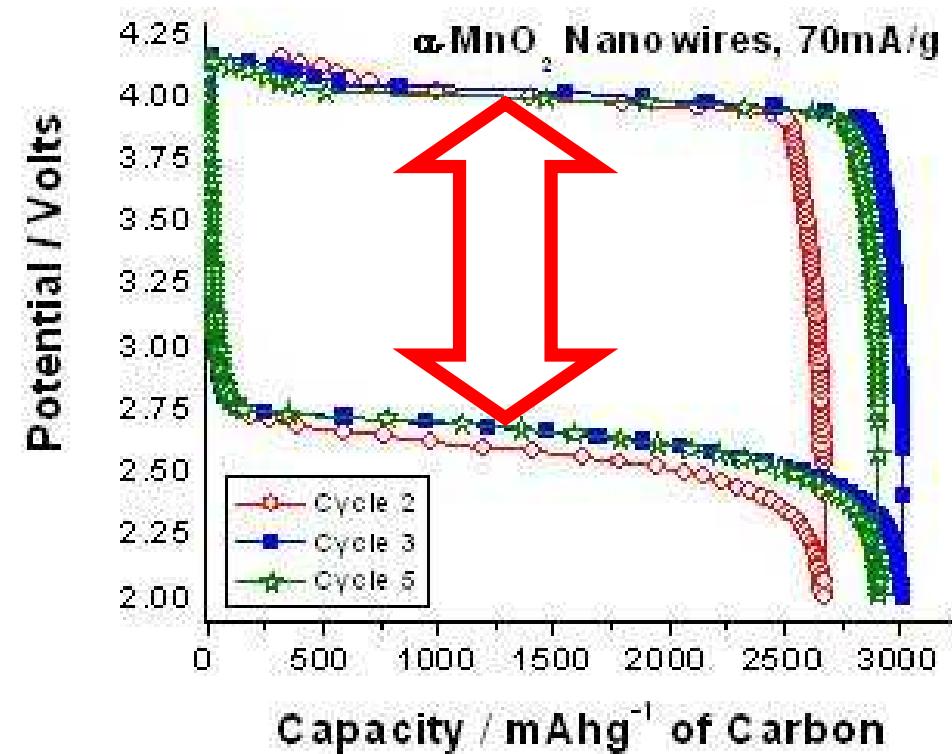
$\Rightarrow \underline{\text{2000 Wh/kg}}$

This is the
maximum for
an ideal
chemistry!

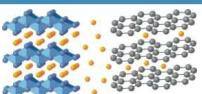


And the ENERGY EFFICIENCY?

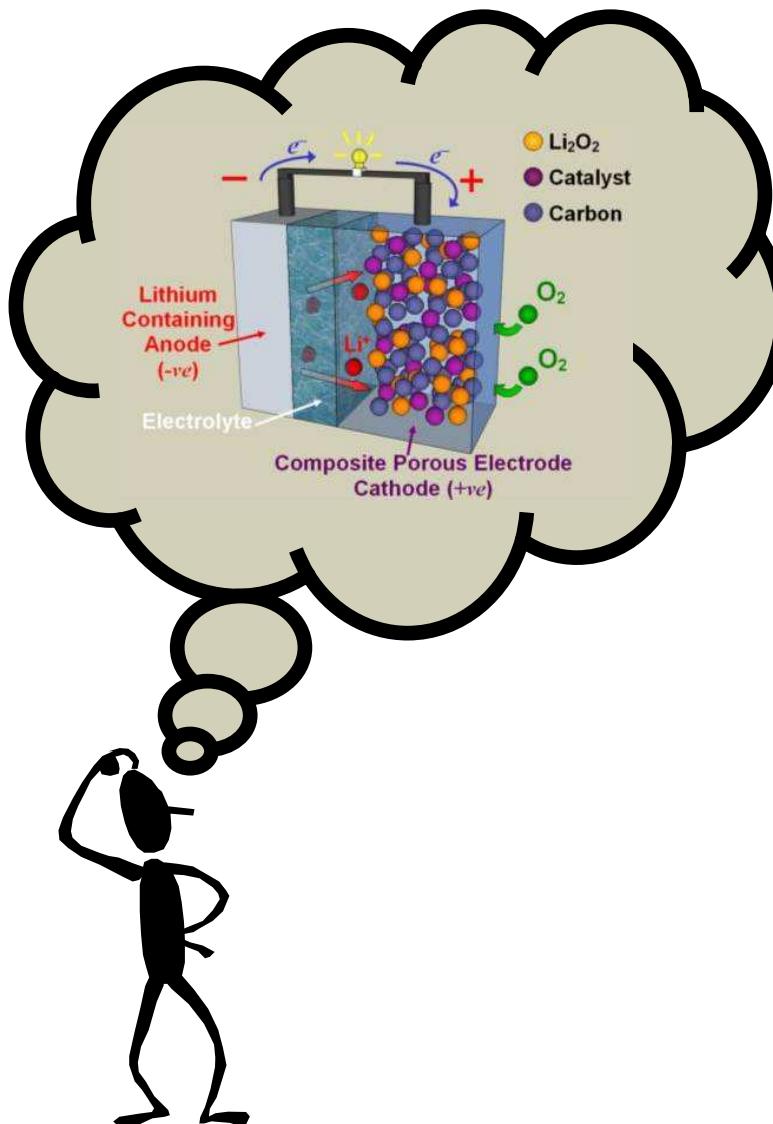
30% of the stored energy is “LOST”!!!



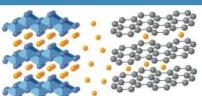
T. Ogasawara, A. Débart, M. Holzapfel, P. Novák, and P. G. Bruce, J. Am. Chem. Soc. 2006 (128), p. 1390



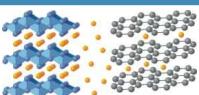
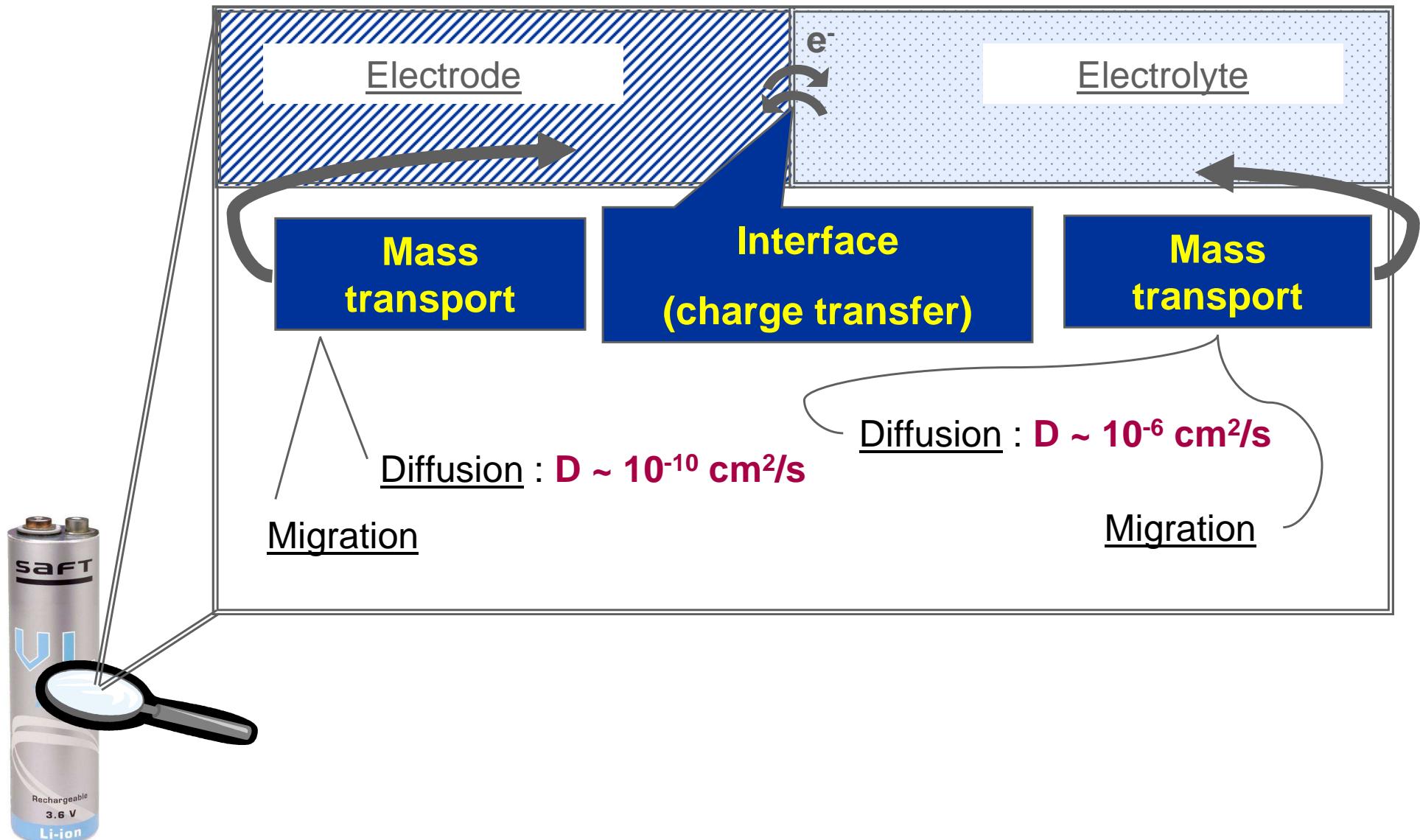
Air, Sulfur, Lithium, ...



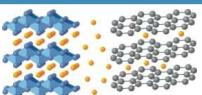
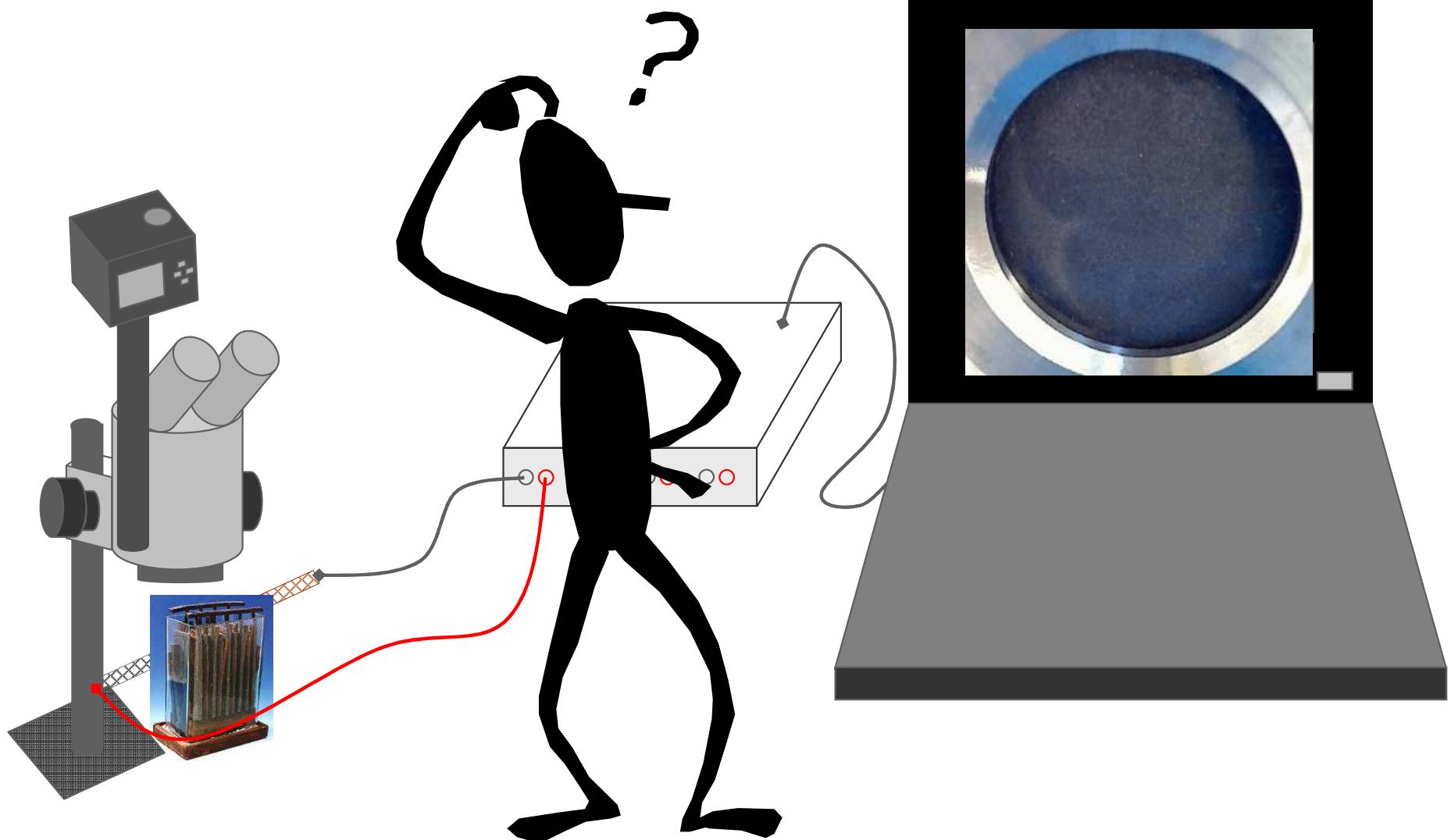
- Great, they are cheap!
- Safe?



We HAVE TO Understand All Processes Inside!

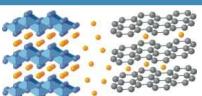
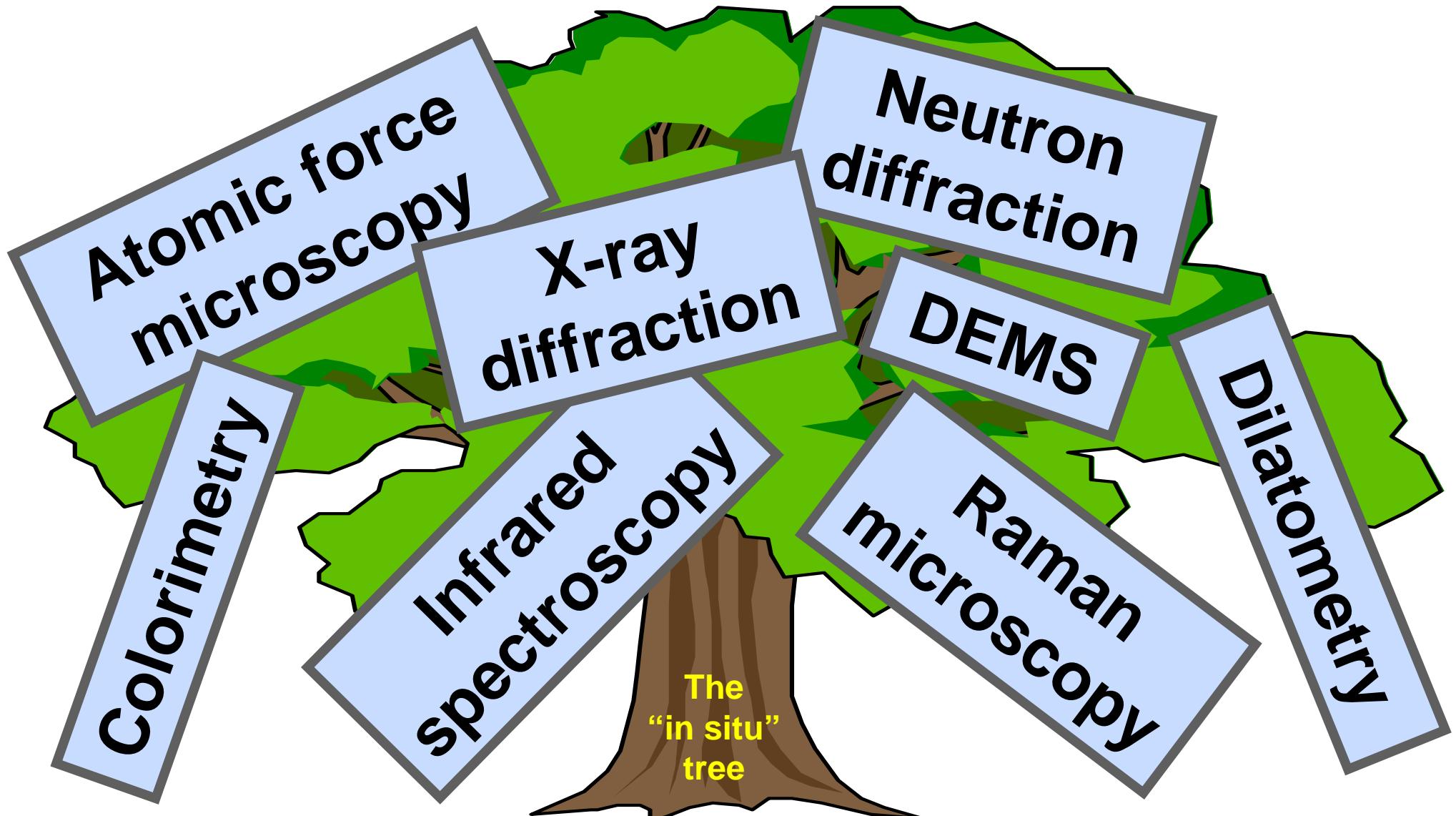


Scientific Look into Batteries



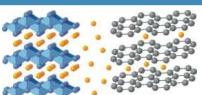
Electrochemical Energy Storage Section

In Situ Characterization of Battery Electrodes

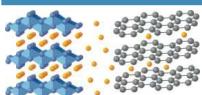
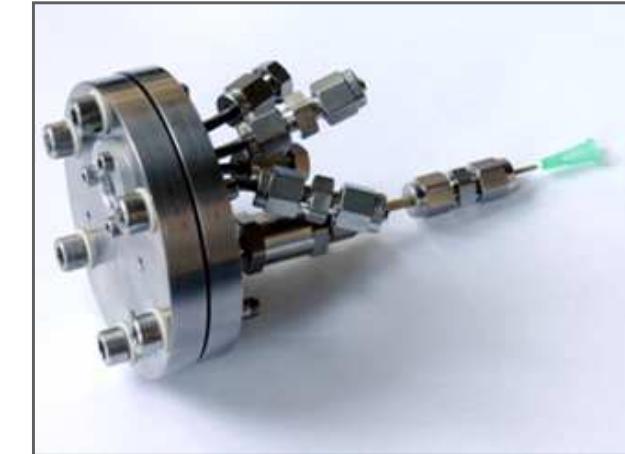
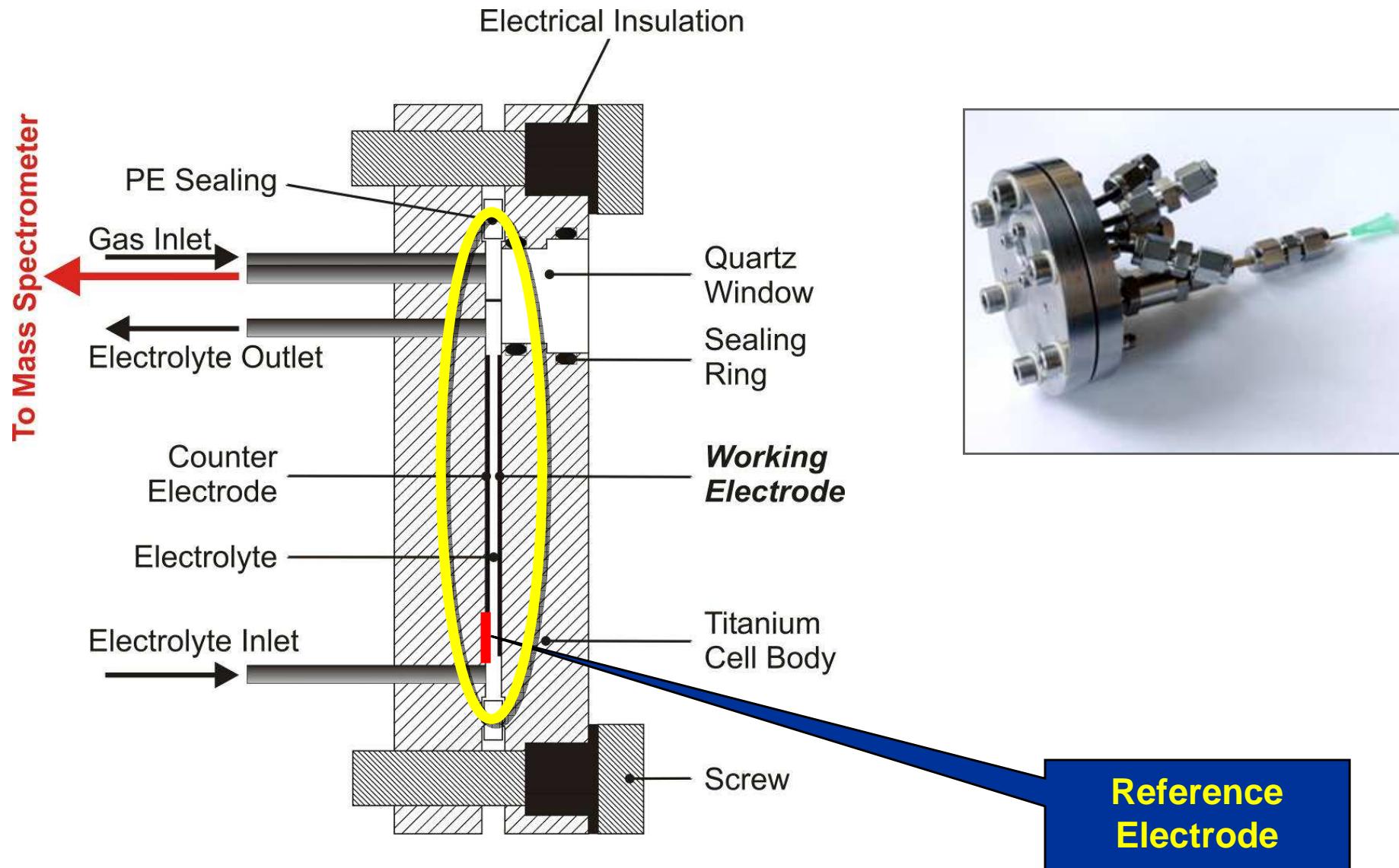


The Characterization Challenge (II)

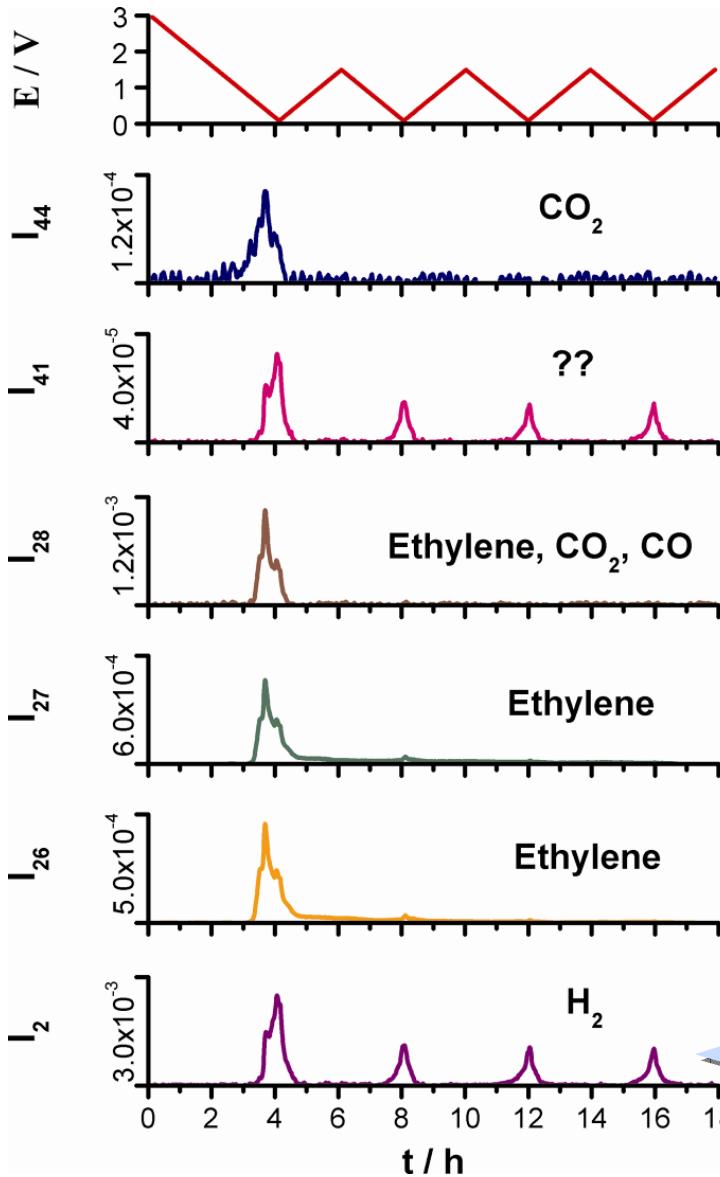
The Lithium–Oxygen Cell



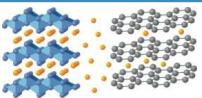
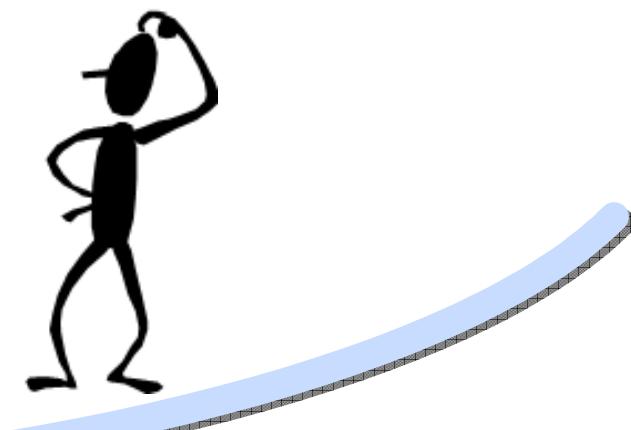
Differential Electrochemical Mass Spectrometry



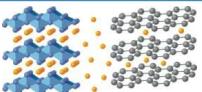
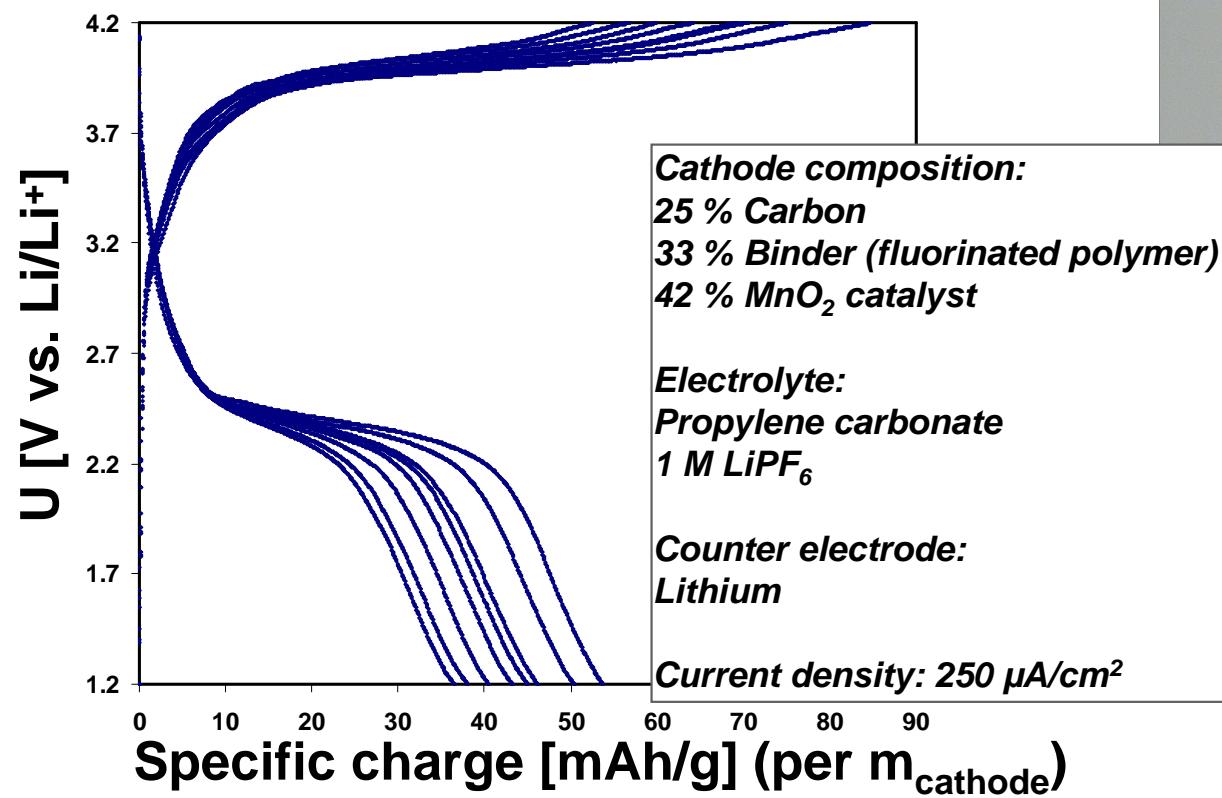
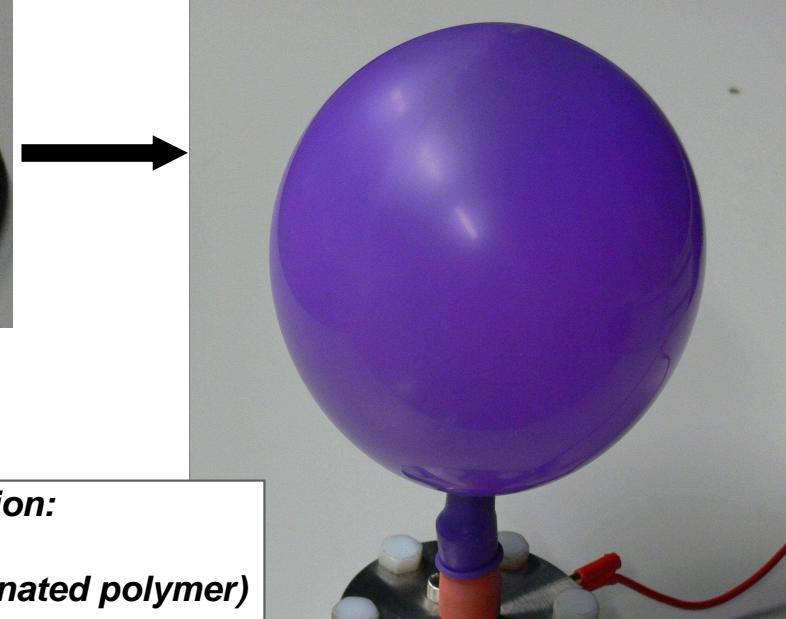
DEMS – How Does It Work?



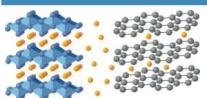
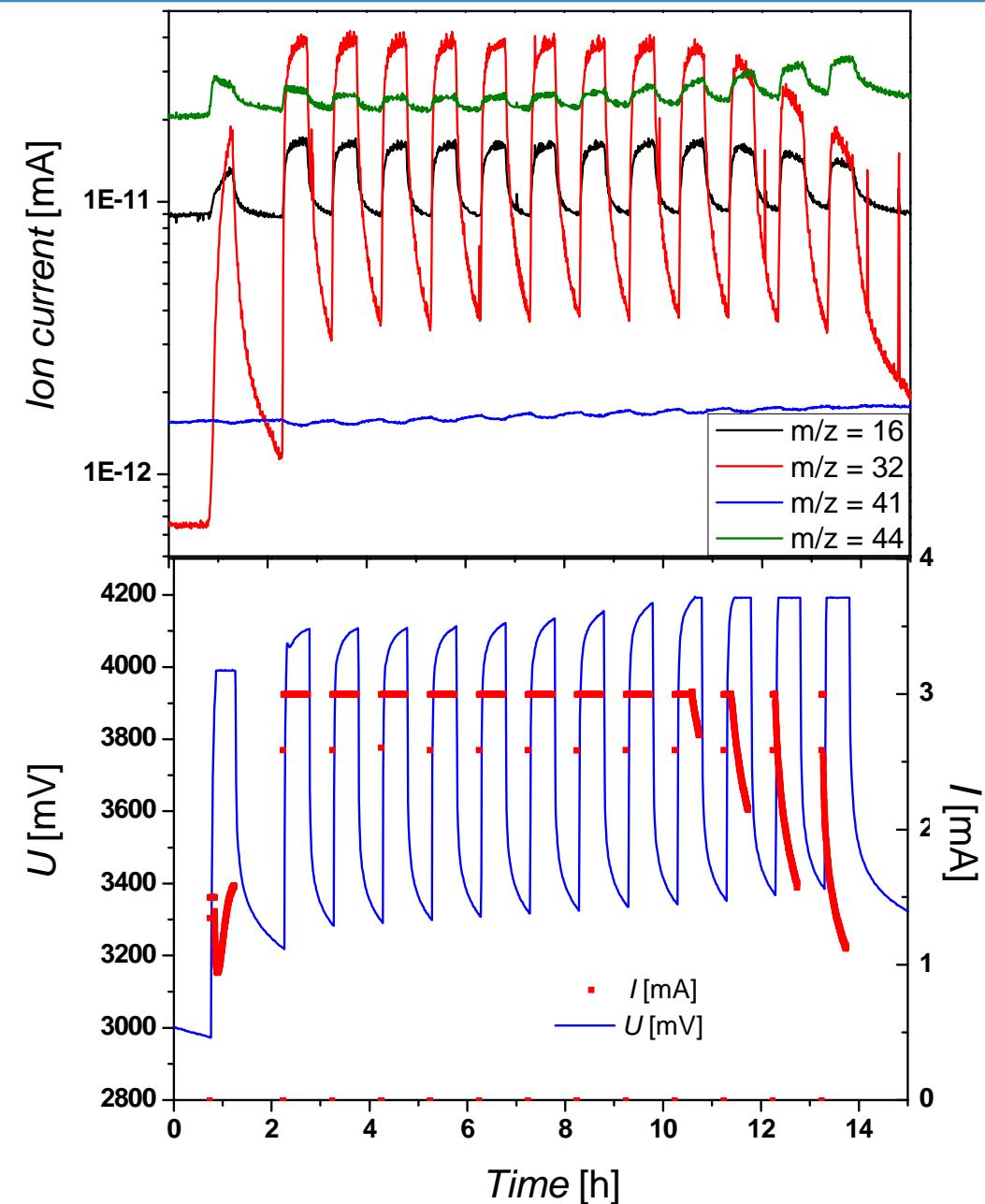
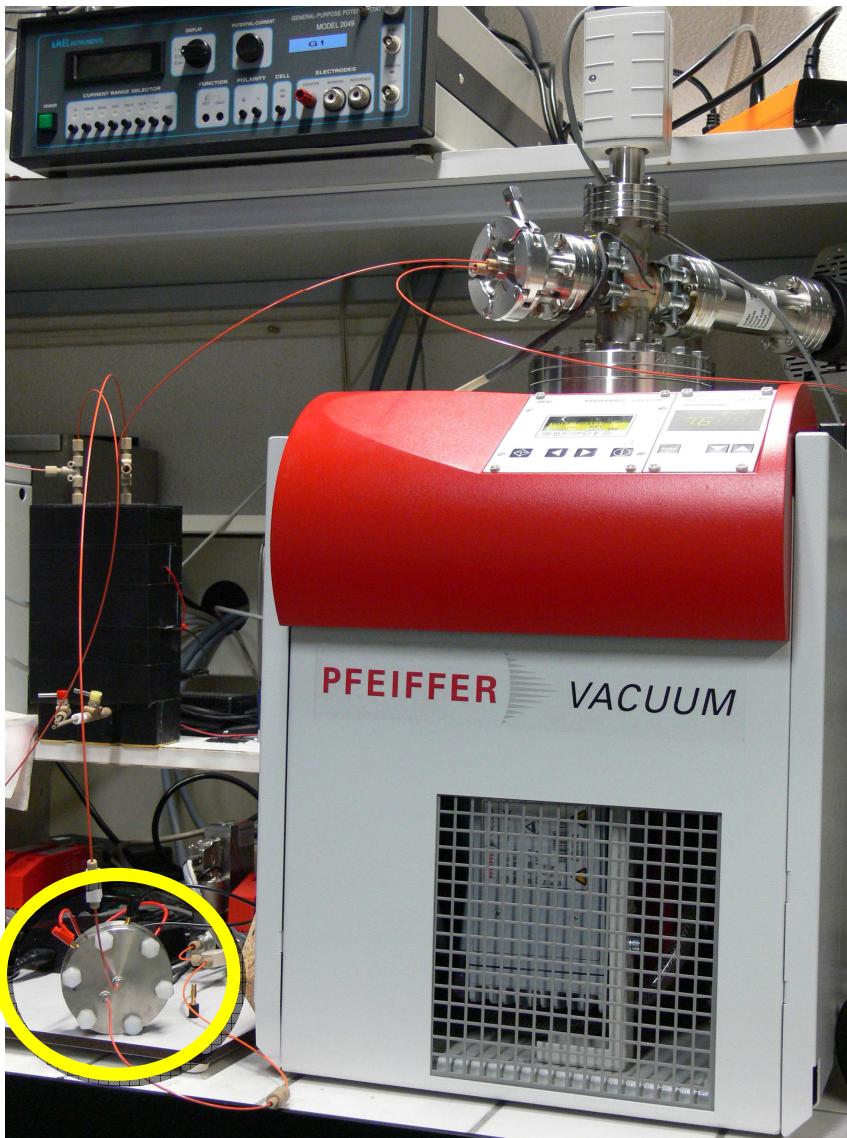
- **TIMREX® KS44 Graphite**
- **1M LiPF₆, EC:DMC (1:1)**
- **3-electrode system**
- **(Li metal = Ref. electrode)**
- **0.09-1.50 V vs. Li/Li⁺**
- **CV @ 0.2 mV/s**



The Lithium–Oxygen Cell

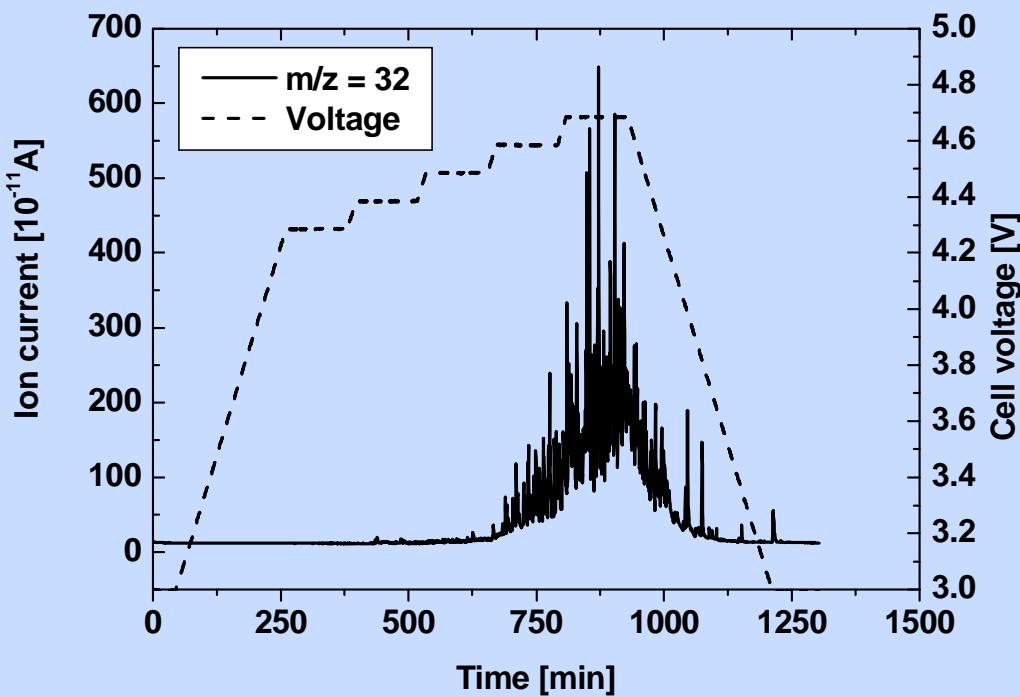


DEMS: $\text{Li}_2\text{O}_2 \rightarrow \text{O}_2 + \text{Li}_2$

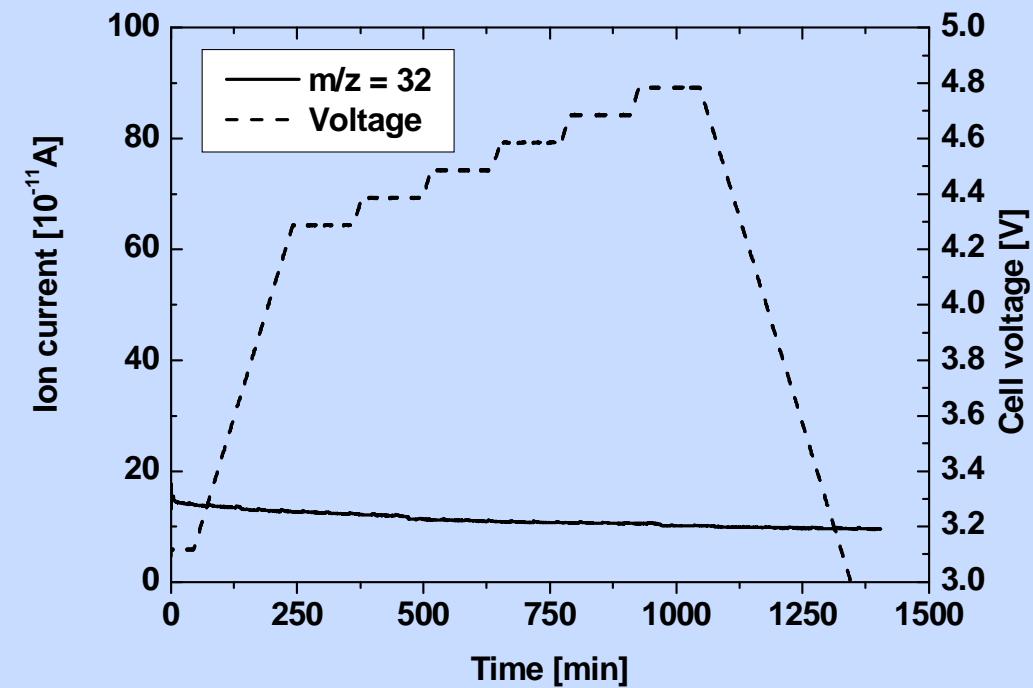


(1995) DEMS: $\text{Li}_2\text{O}_2 \rightarrow \text{O}_2 + \text{Li}_2$

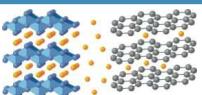
electrode with Li_2O_2



electrode without Li_2O_2

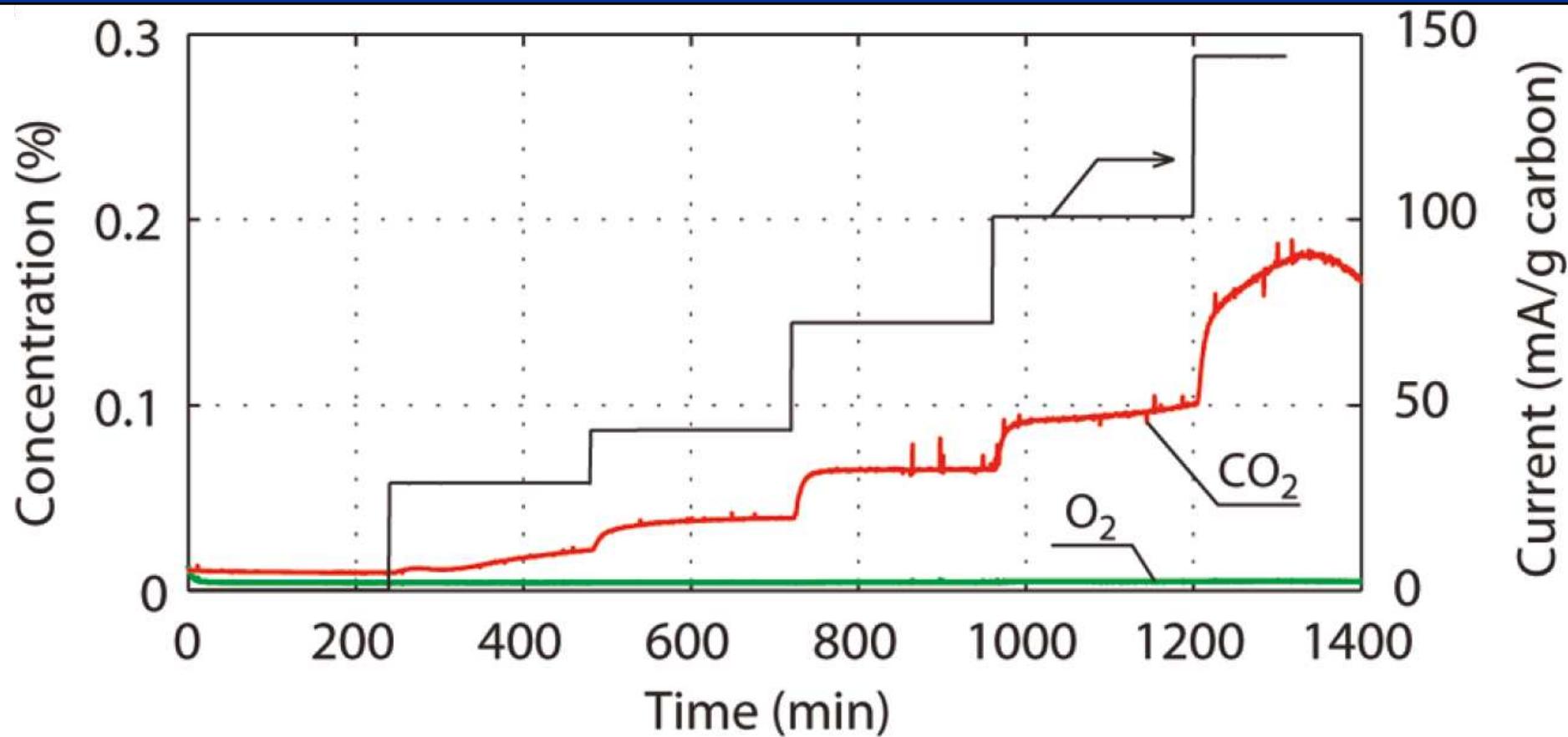


T. Ogasawara, A. Débart, M. Holzapfel, P. Novák, and P. G. Bruce, J. Am. Chem. Soc. 2006 (128), p. 1390

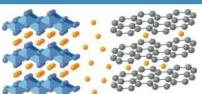


(2000) DEMS: Reactions in the Lithium-O₂ Battery

oxidation of a composite electrode containing Li₂CO₃ in response to a stepwise increased current under Ar

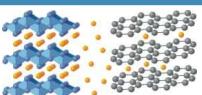


S. A. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Bardé, P. Novák, and P. G. Bruce,
J. Am. Chem. Soc., available on web (2011). - doi:10.1021/ja2021747



The Characterization Challenge (III)

The Lithium–Sulfur Cell



The Lithium–Sulfur Cell

Sulfur is cheap, abundant, and environmentally benign...

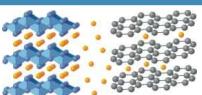


Li-S battery:

Specific Charge: $\leq 1170 \text{ Ah/kg}$ (Li_2S)

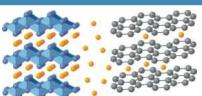
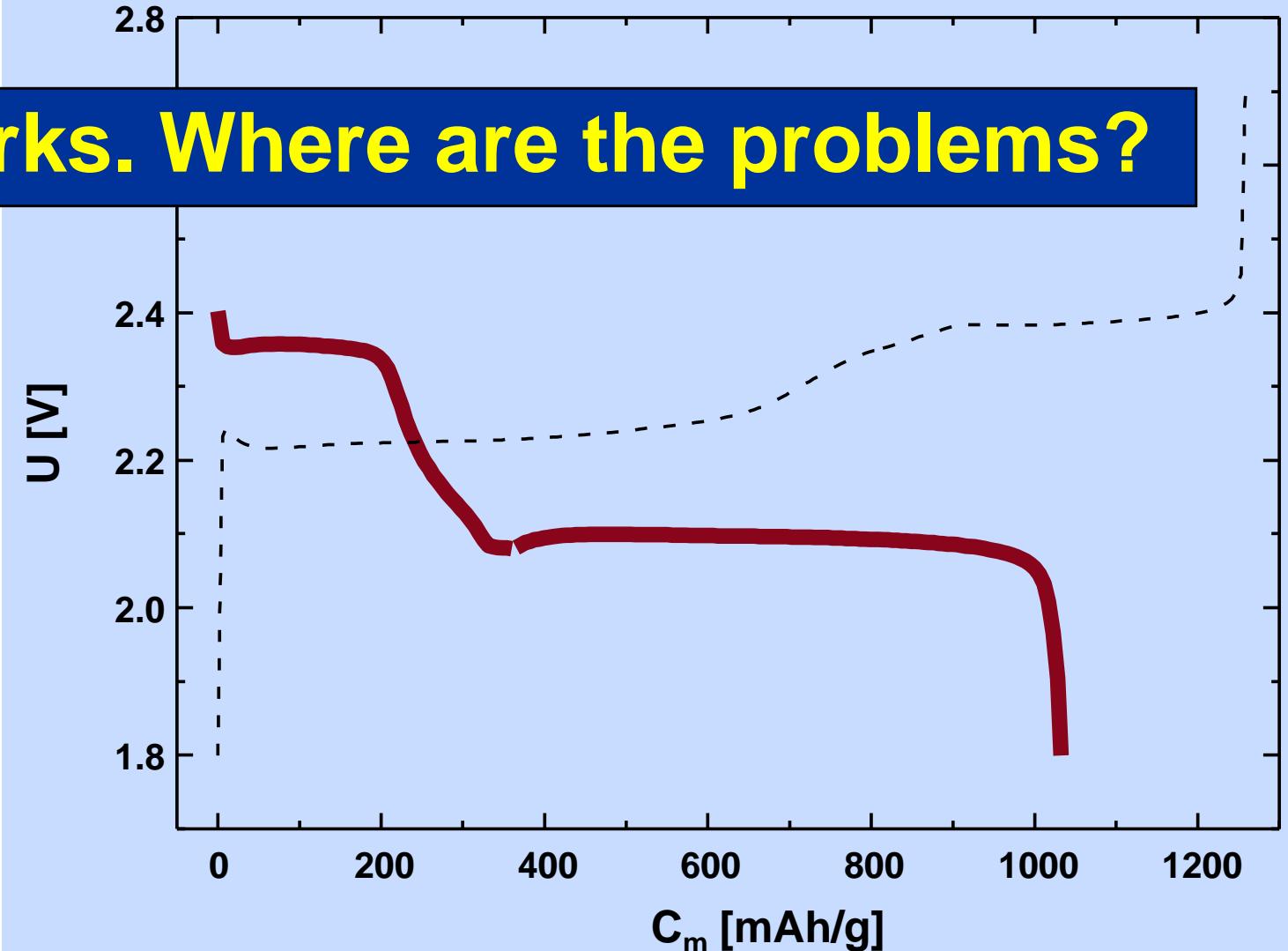
Specific Energy: $\sim 2500 \text{ Wh/kg}$

$\Rightarrow 2500 / 4 = 625 \text{ Wh/kg}$ for the “real” battery



The Lithium–Sulfur Cell

OK; it works. Where are the problems?



The Lithium–Sulfur Cell

Sulfur: Insulator

(Conductivity: $5 \cdot 10^{-14}$ S/cm)

Aging of electrodes

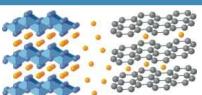
(e.g., by formation of inactive precipitates such as Li_2S and Li_2S_2)

Dendrite formation

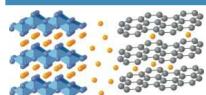
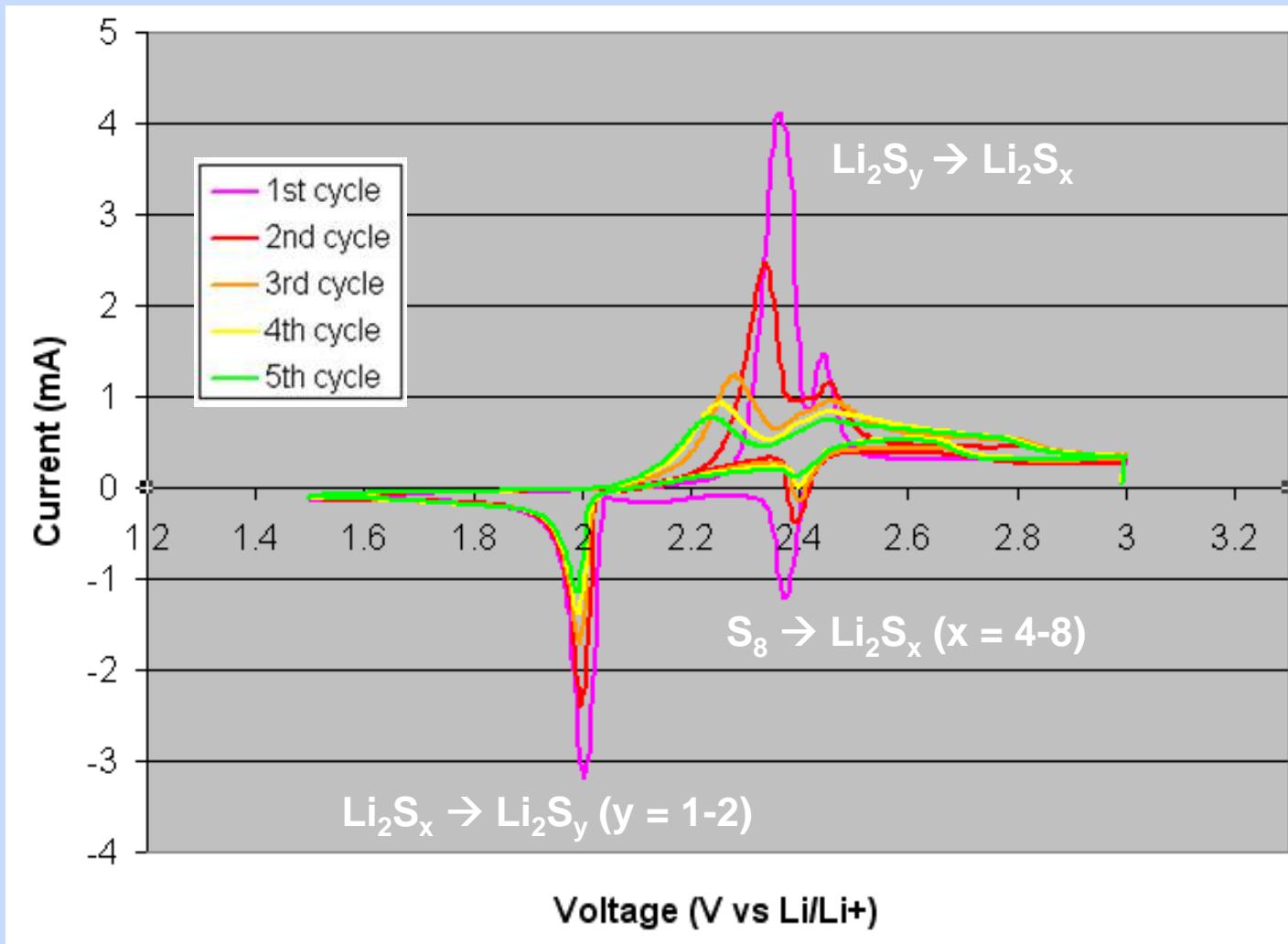
(if Li metal is used as anode material)

Problems

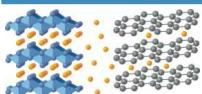
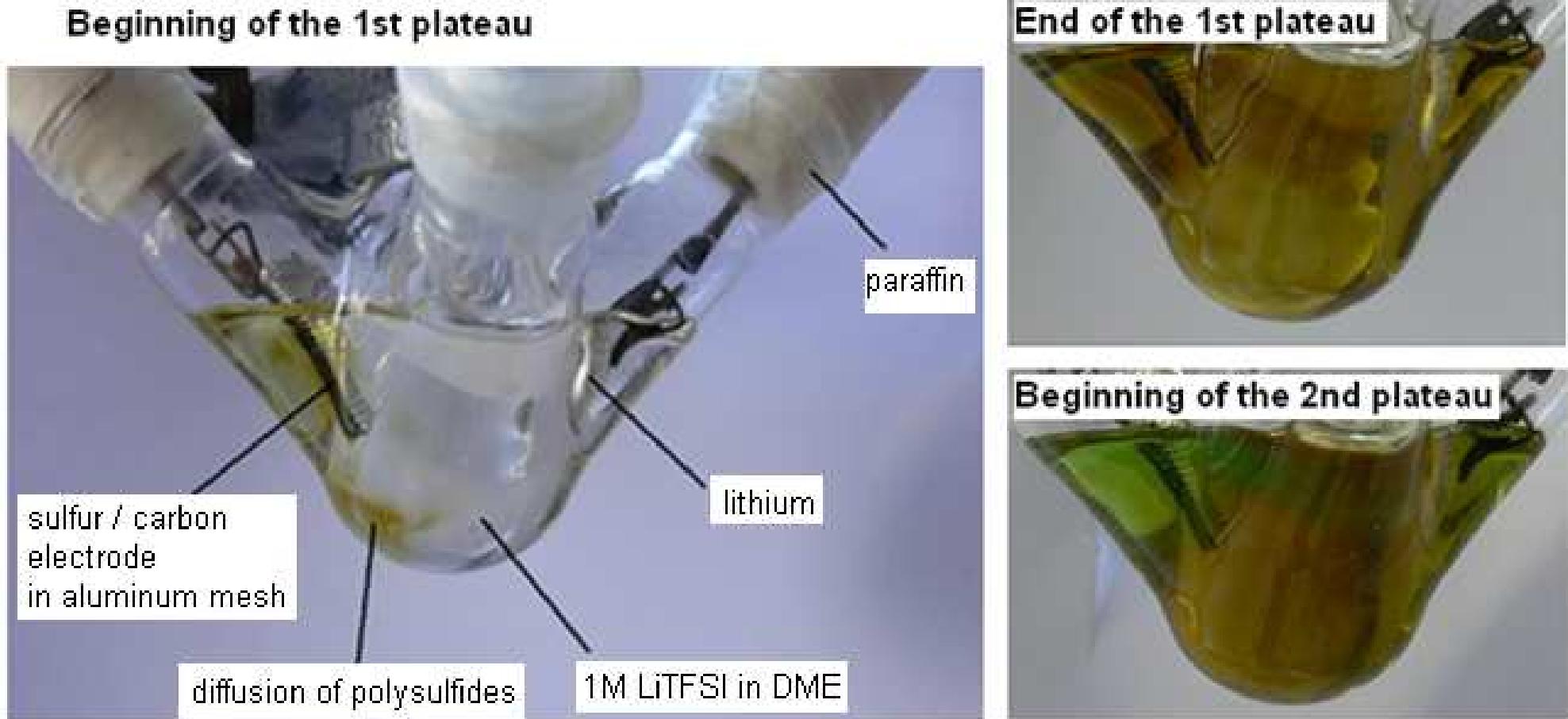
Polysulfide shuttle



The Lithium–Sulfur Cell: Standard Separator

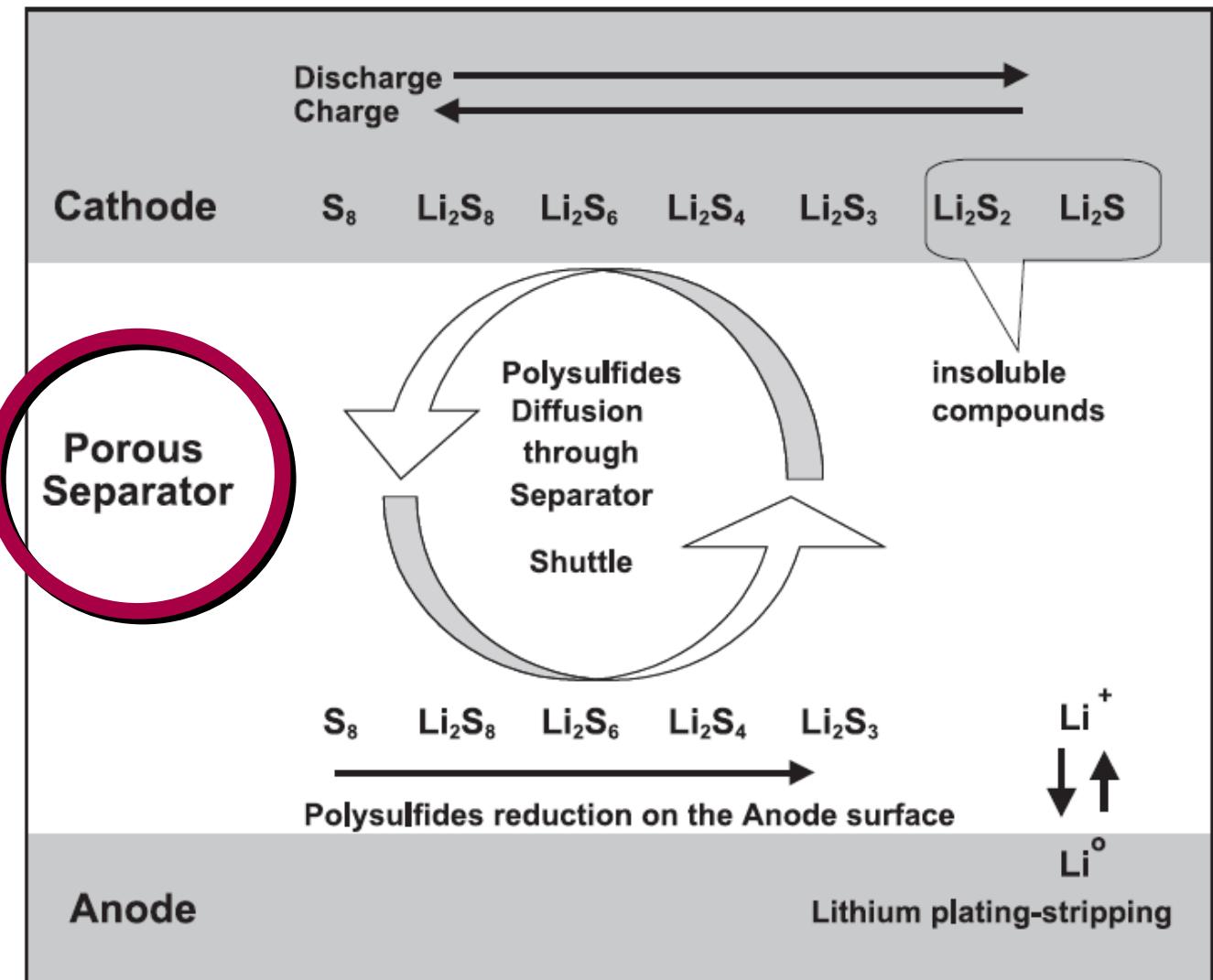


The Lithium–Sulfur Cell: No Separator

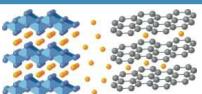


The Lithium–Sulfur Cell

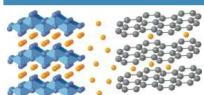
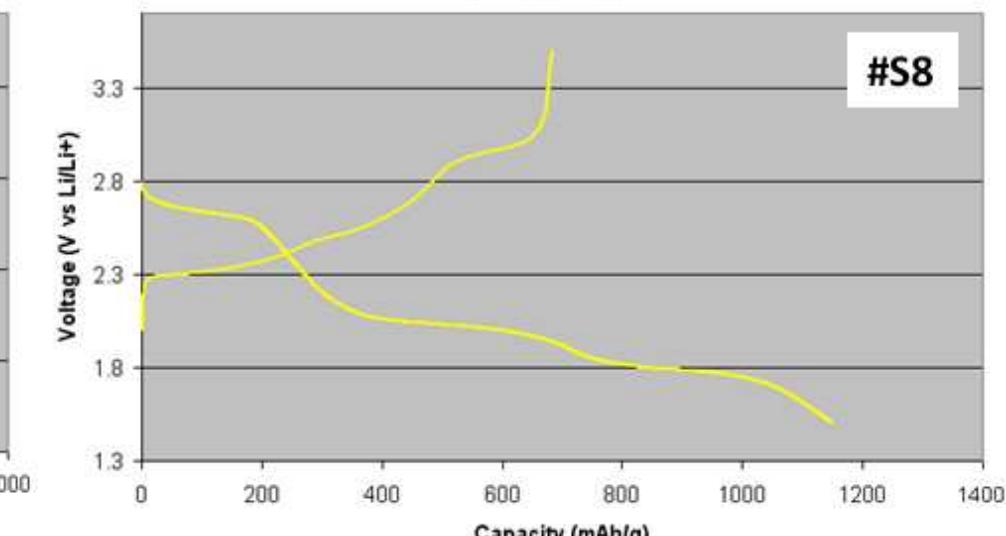
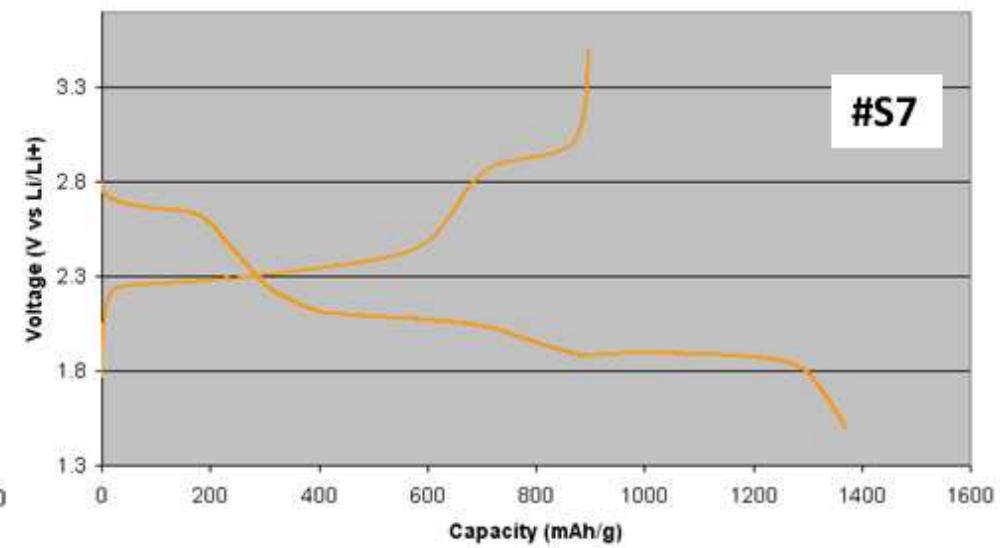
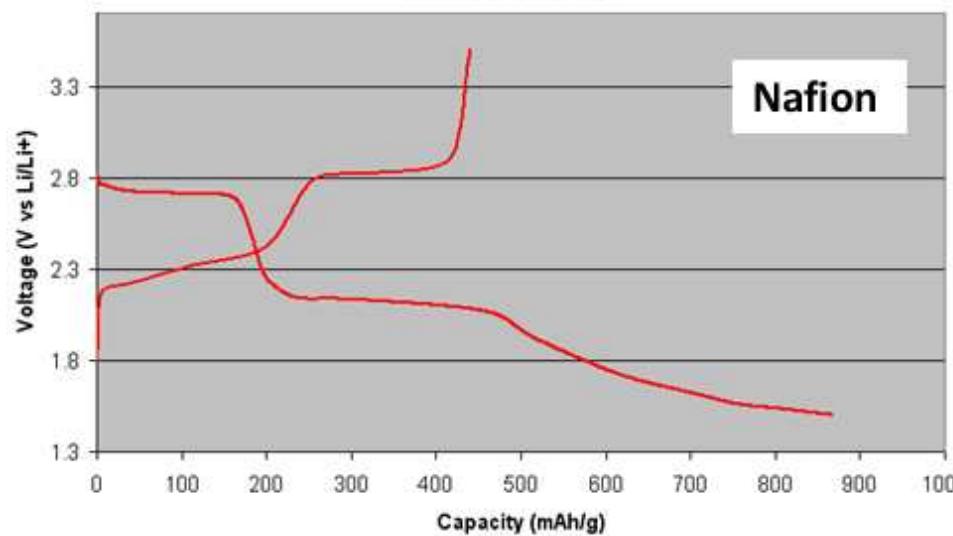
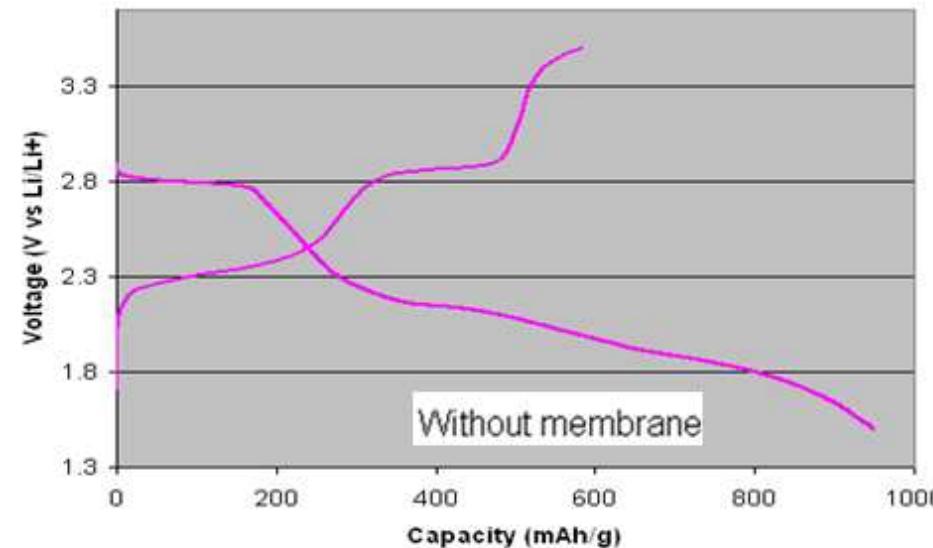
Add a membrane!



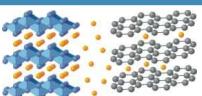
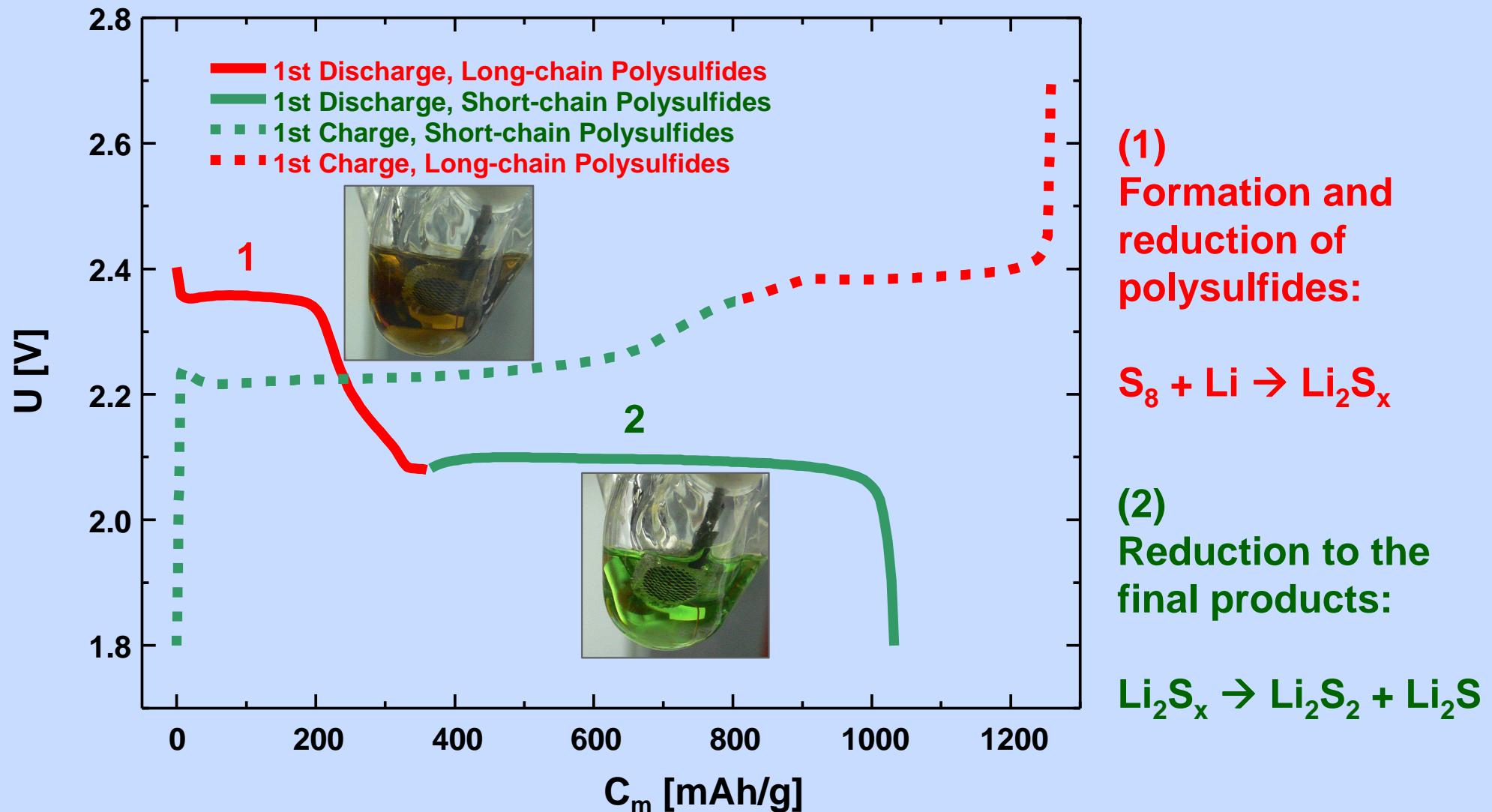
Akridge et al., Solid State Ionics, 175, 243, 2004



Li^+ -Conducting Membrane: Proof of Concept

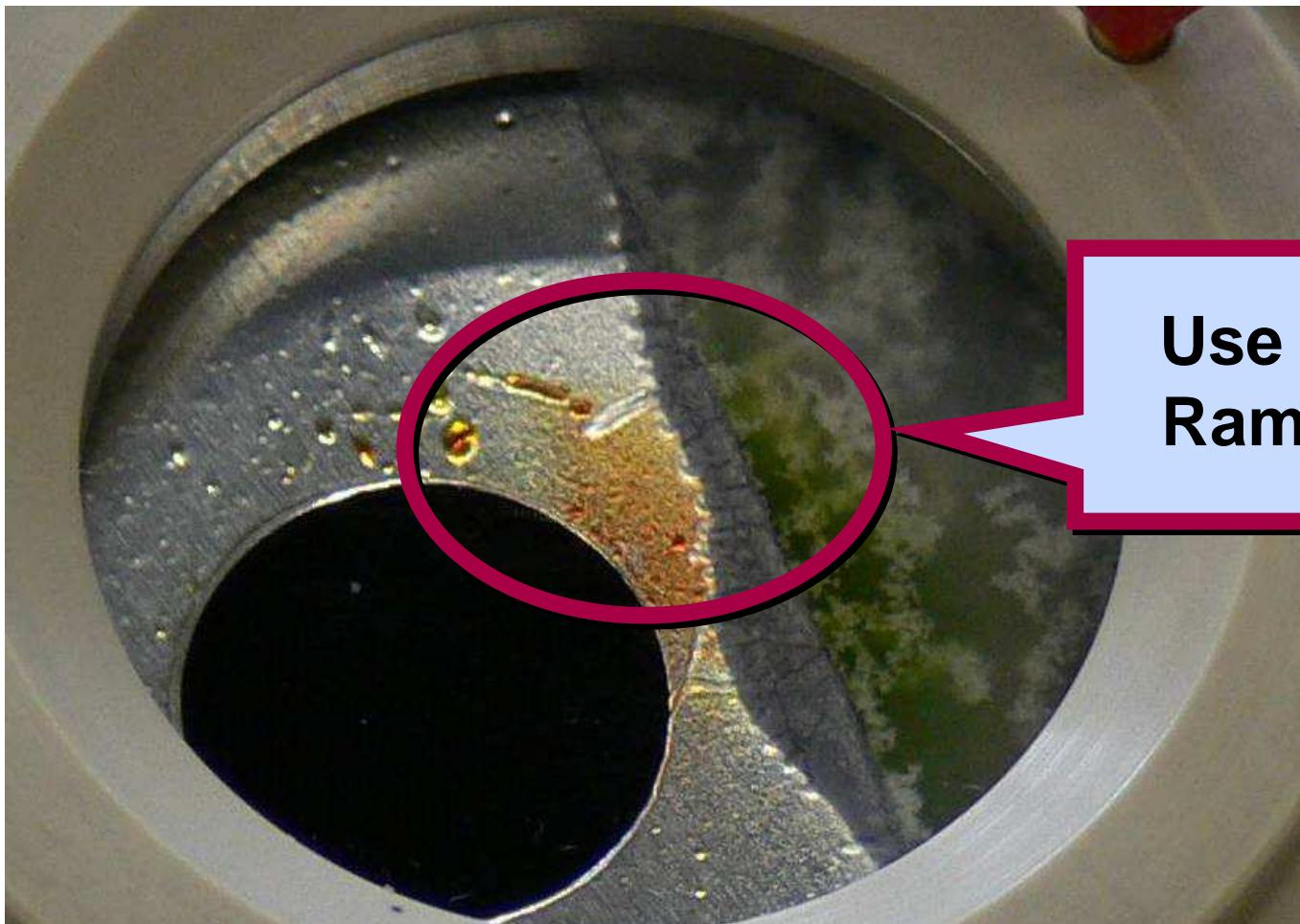


The Lithium–Sulfur Cell: Standard Separator

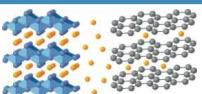


The Lithium–Sulfur Cell

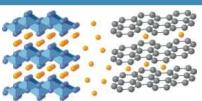
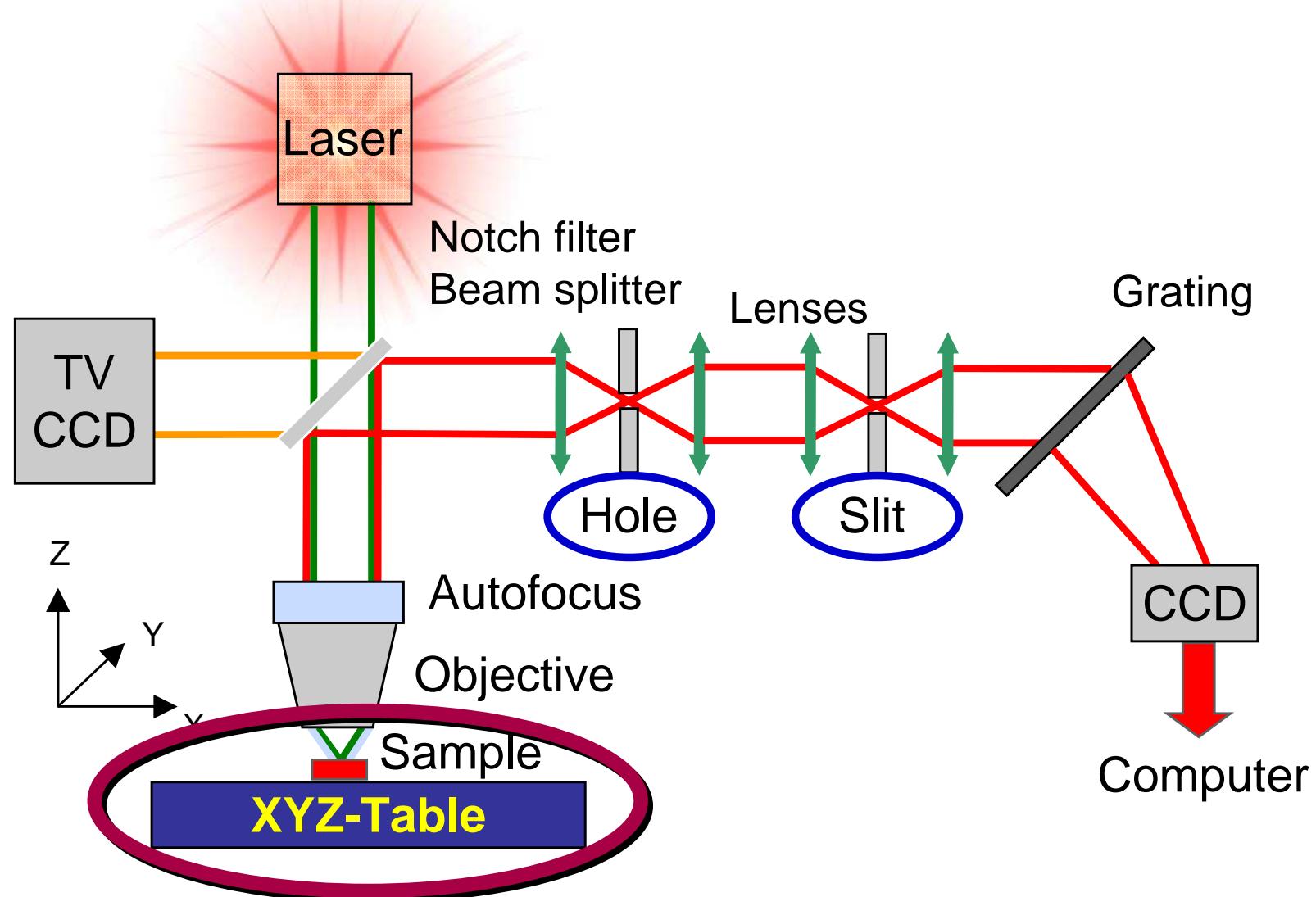
**Sulfur–carbon electrode in an LiPF_6 / triglyme electrolyte
after shortcircuiting with a lithium anode.**



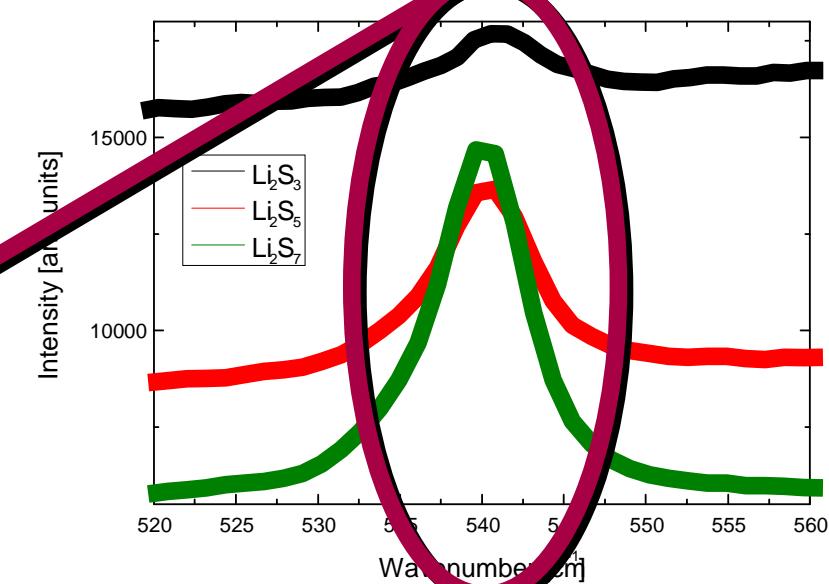
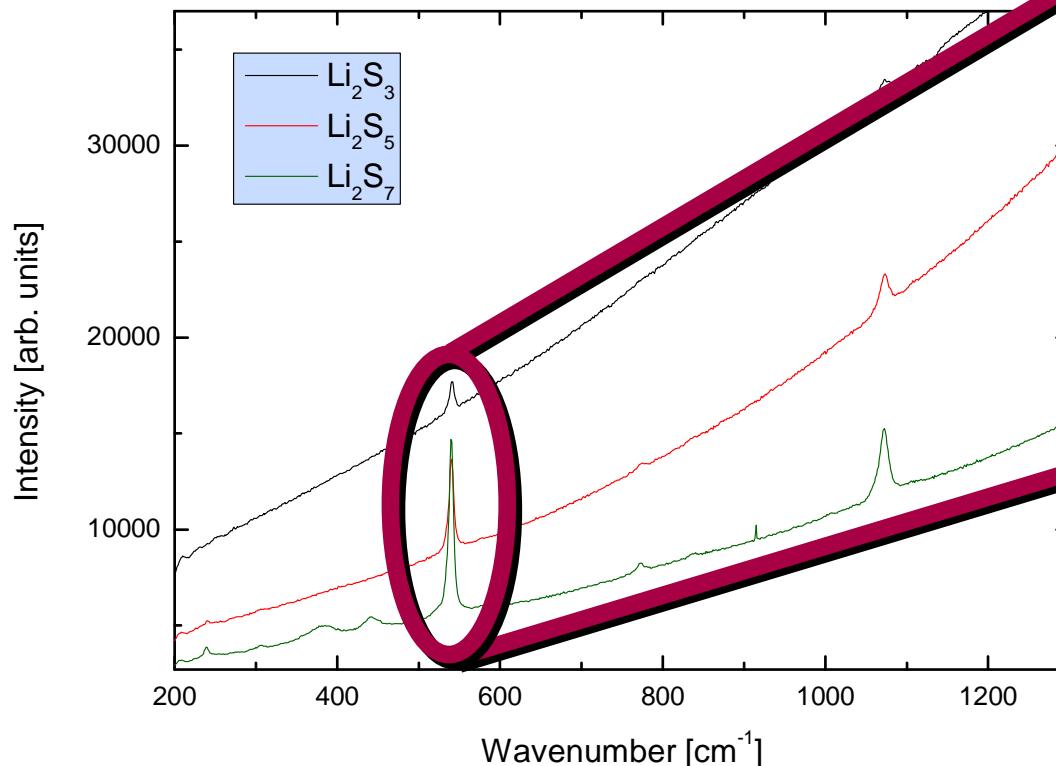
**Use colorimetry and
Raman microscopy!**



Confocal Raman Microscopy

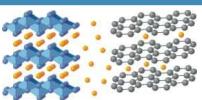


Raman Spectroscopy of Polysulfide Solutions

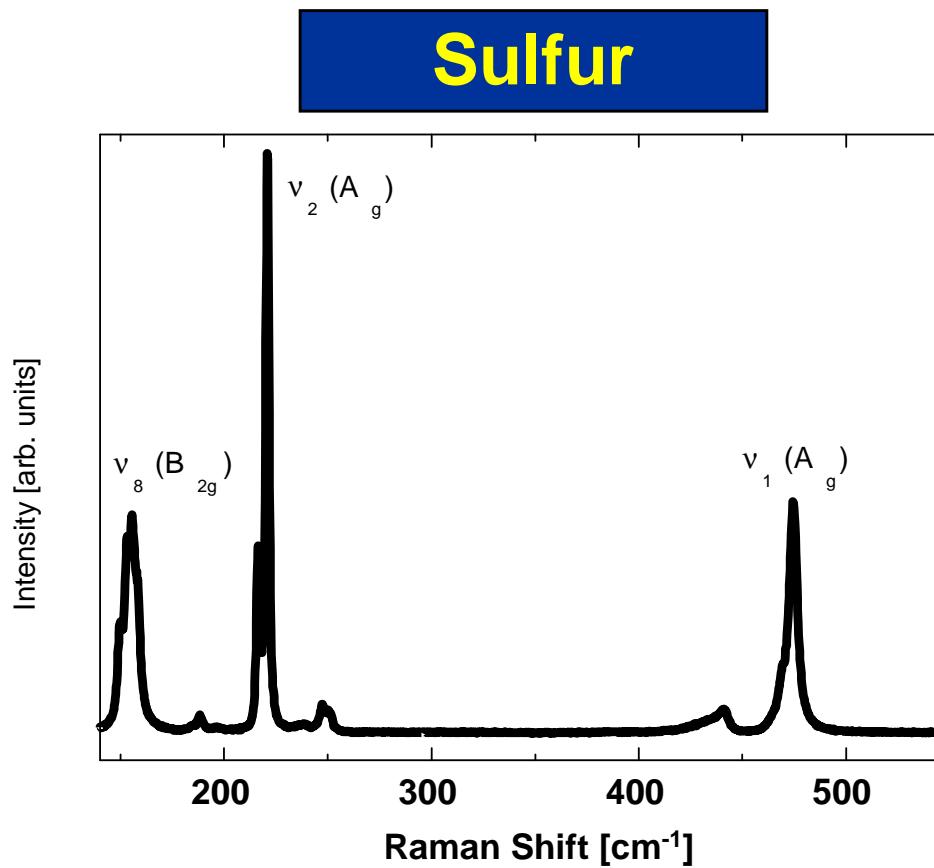


No significant shift in peak positions observable

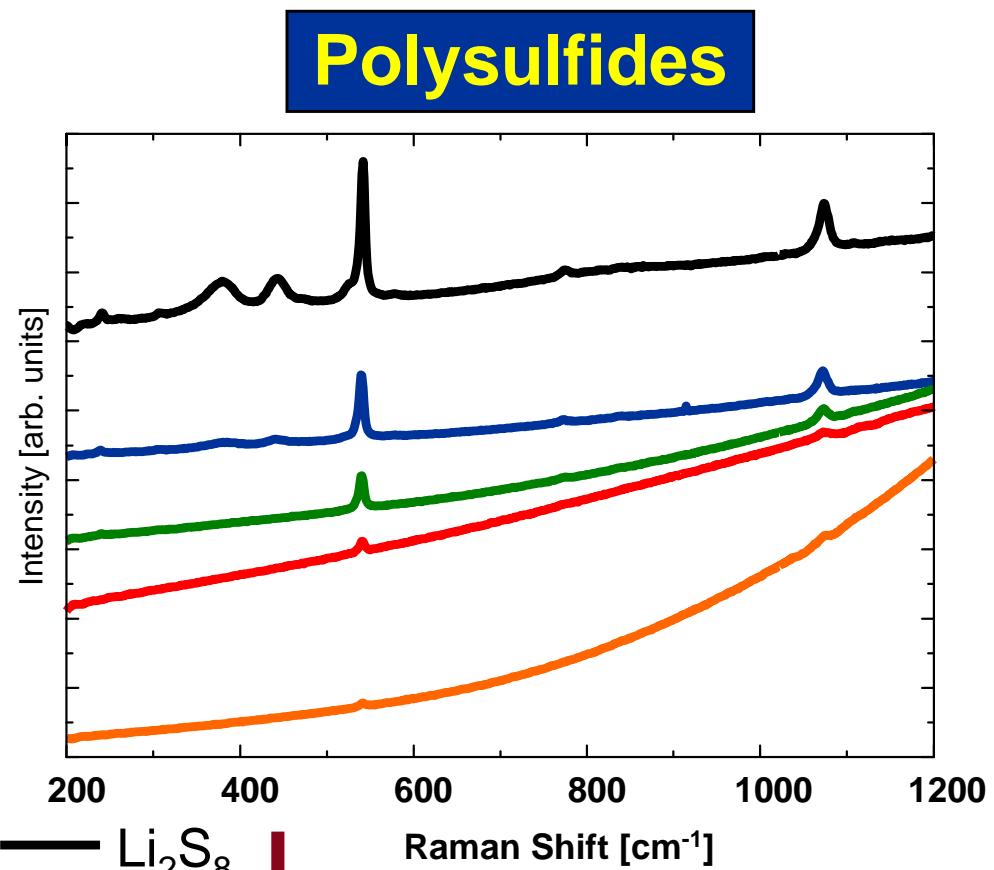
Solutions prepared by Robert Bosch GmbH



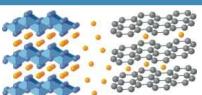
Raman Spectroscopy: The Markers



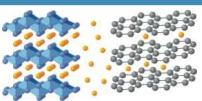
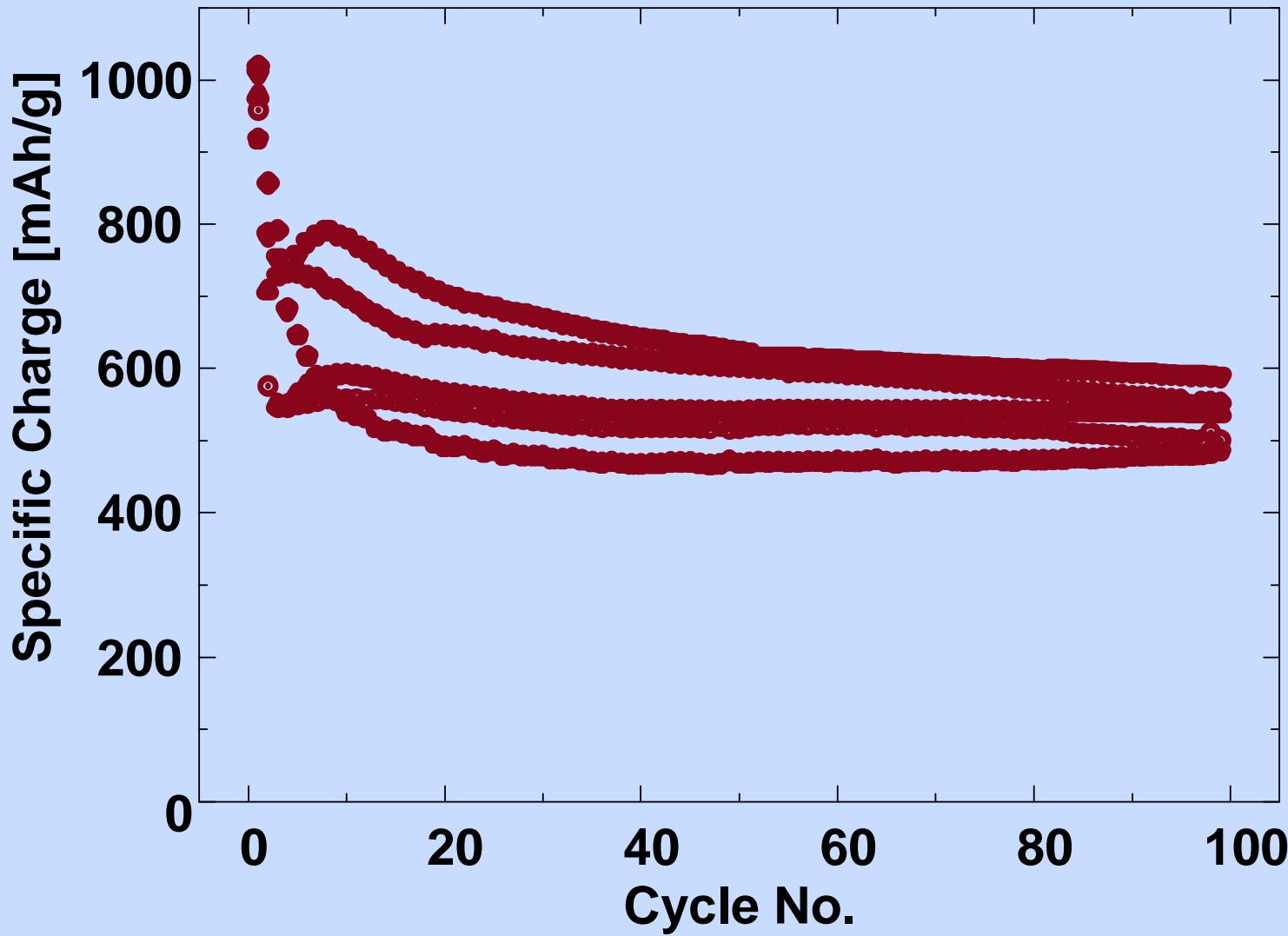
“Inactive” sulfur detectable



Decrease in signal intensity
with decreasing chain
length of S_x^{2-} anions

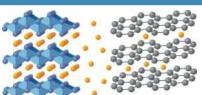


The Lithium–Sulfur Cell: Where Are We?



Conclusion

- Development of *in situ* methods is pure fundamental research...
- ...but it helps to avoid future problems in the battery industry.



Acknowledgments



- *BASF SE, Ludwigshafen, Germany*
- *TIMCAL SA, Bodio, Switzerland*
- *Swiss National Science Foundation*
- *European Community*
- *my group*



- *and numerous former group members, other colleagues, and friends!*

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