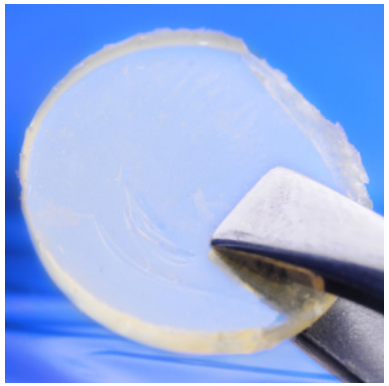
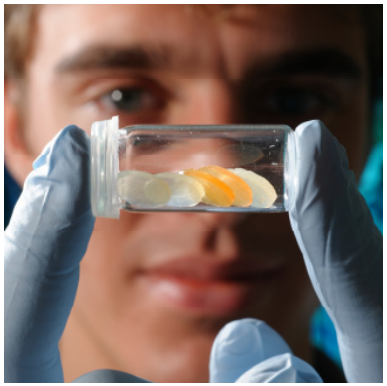
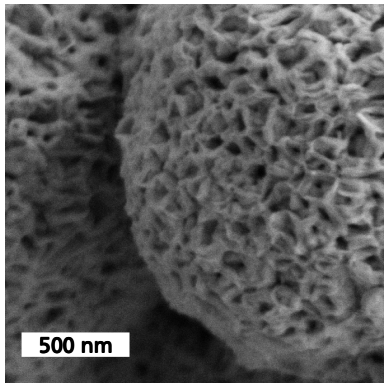
Elektrolyte in Li-Akkus - Stand der Technologie und deren Weiterentwicklung

Kai-C. Möller







materials valley

Workshop „*Elektrochemische Energie-Speicher- und -Wandlersysteme*“, 11. Februar 2010, Industriepark Wolfgang, Hanau

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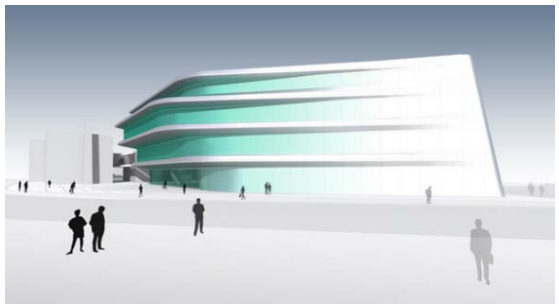
Elektrolyte in Li-Akkus - Stand der Technologie und deren Weiterentwicklung



Kai-C. Möller

Competence Team Manager
Electrochemical Energy Storage and Conversion

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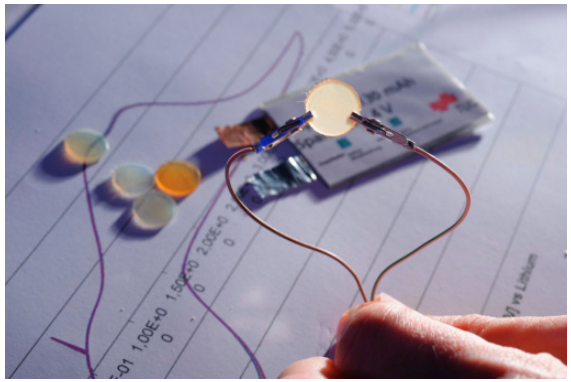
Inhalt

Einleitung

flüssige Elektrolyte

- Anforderungen
- (Haupt-)Bestandteile
- *in situ*-Untersuchungsmethoden
- Elektrolytaddive
- Separatoren



Polymer- / Polymer-Gel-Elektrolyte

Marktübersicht Elektrolythersteller

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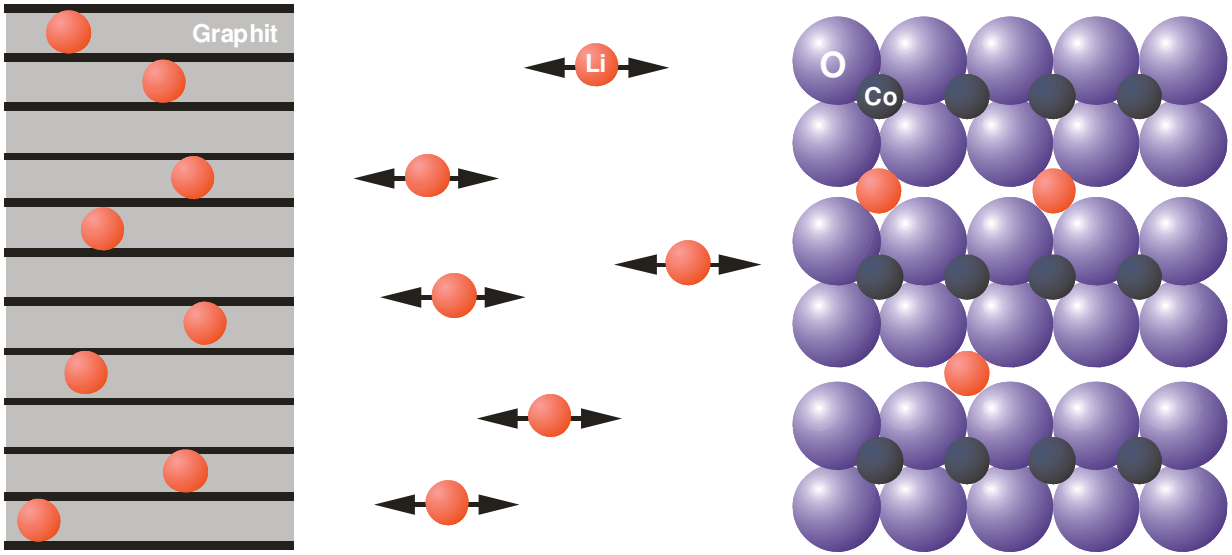
Lithium-Ionen-Batterie – Aufbau

Einlagerungsverbindungen = Wirtsmaterialien für Lithium-Ionen



Negative - "Anode"

Positive - "Kathode"

$$Li_xC_n \rightleftharpoons xLi^+ + xe^- + C_n$$

$$Li_{1-x}CoO_2 + xe^- + xLi^+ \rightleftharpoons LiCoO_2$$

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Lithium-Ionen-Batterie – Anforderungen an den Elektrolyten

- gute ionische Leitfähigkeit (> 1 mS/cm)
- hohe Li^+-Beweglichkeit
- weiter Temperaturbereich
- gute elektrochemische Stabilität
- thermische Stabilität
- kompatibel zu anderen Zellkomponenten:
  - Anodenmaterial
  - Kathodenmaterial
  - Separator
  - Stromableiter

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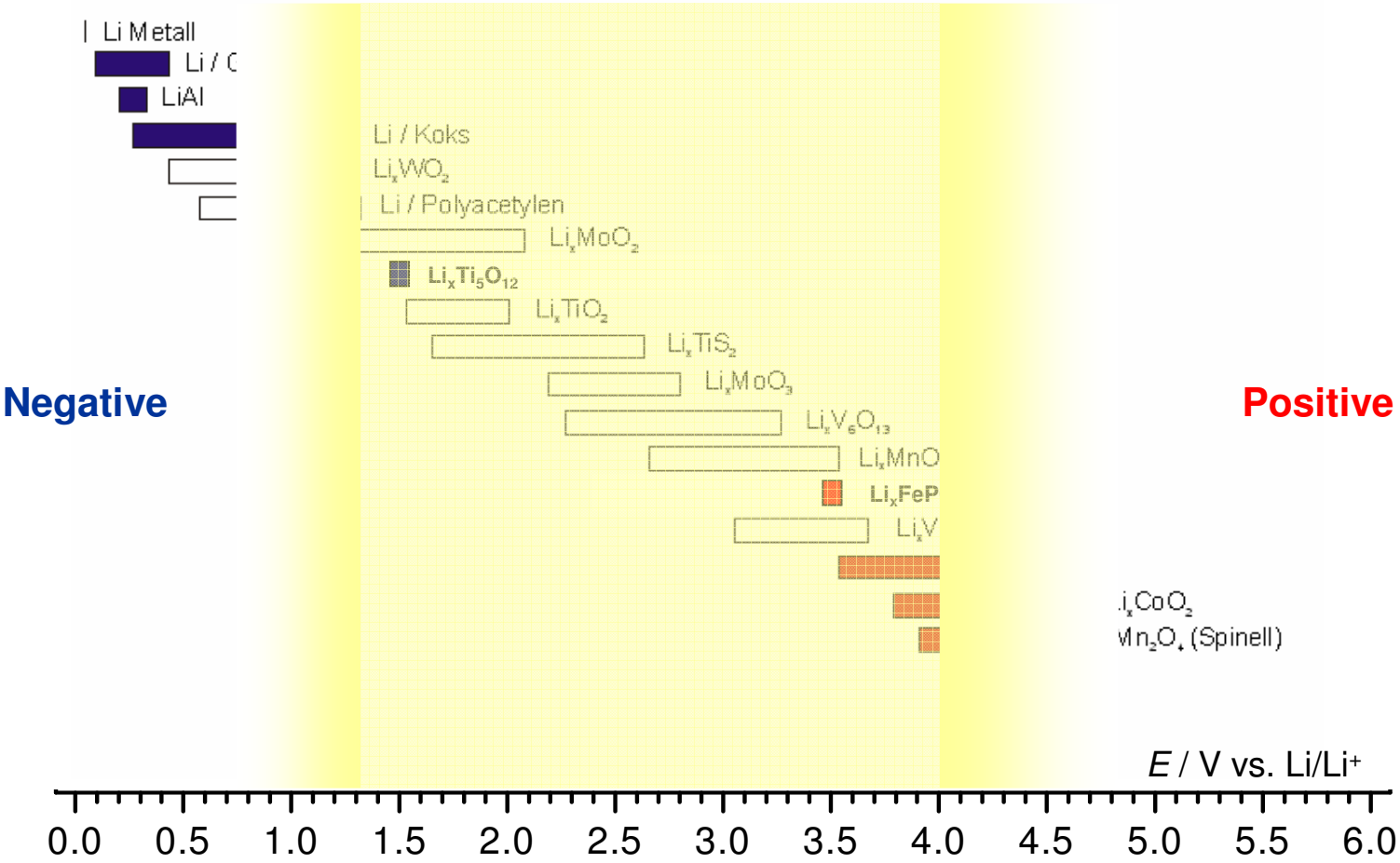
Lithium-Ionen-Batterie – Elektrodenmaterialien



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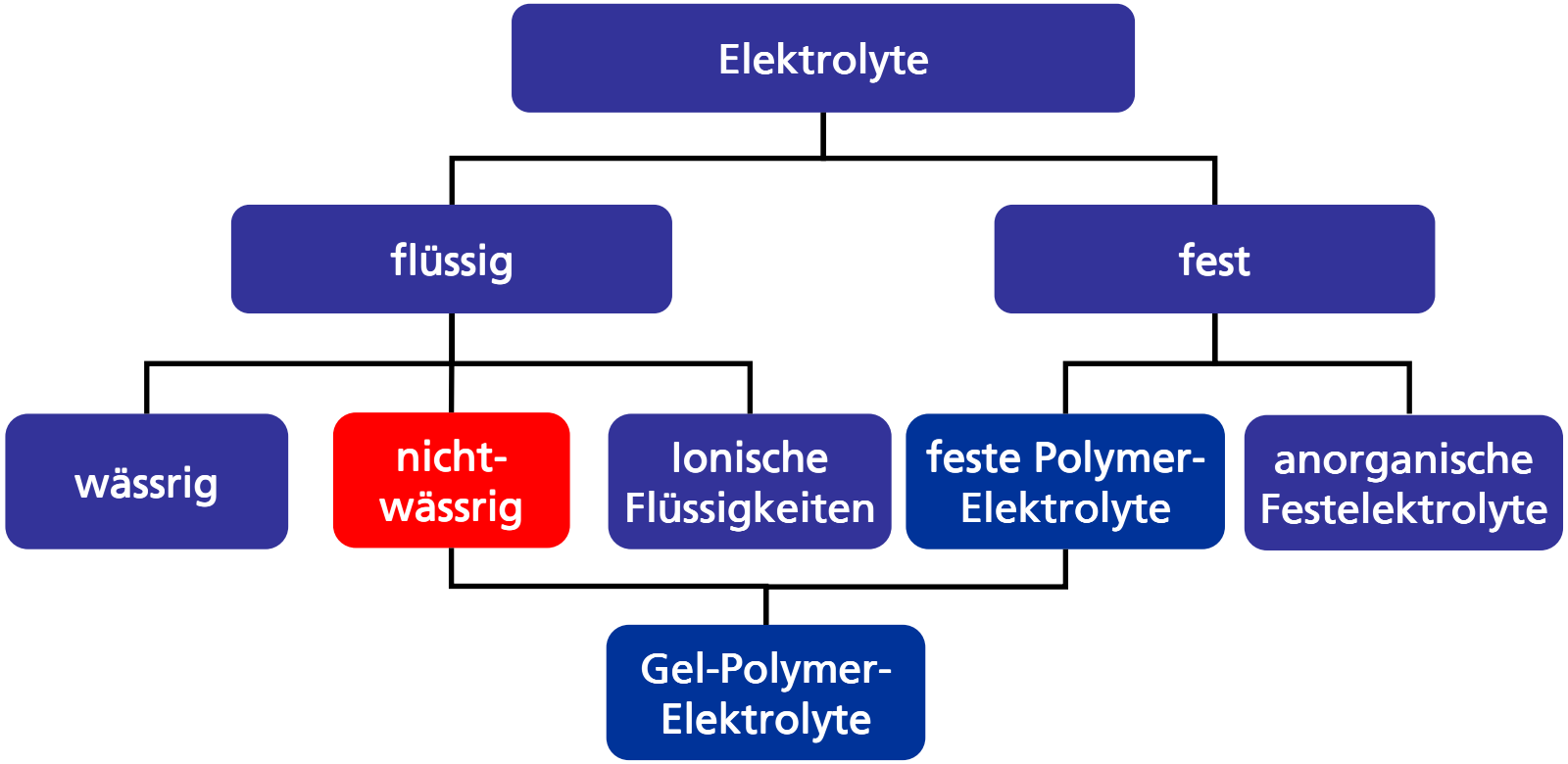
Elektrolyte



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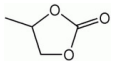
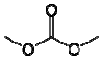
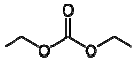
Elektrolyt – Lösemittel

Lösemittel		*Schmp. / °C*	*Sdp. / °C*	*Fl.p. / °C*	*Visc. / mm^2/s[a]*	*ε*
EC		39	248	160	1.86[b]	89.6[b]
PC		-49	240	132	2.5	64.4
DMC		5	91	18	0.59	3.12
DEC		-43	126	72	0.75	2.82
DME		-58	85	1	0.46	7.20
GBL		-43	203	99	1.75	39
AN		-45	81	5	0.34	37.5

[a] 25 °C, [b] 40 °C

Elektrolyt = Lösemittel + Leitsalz

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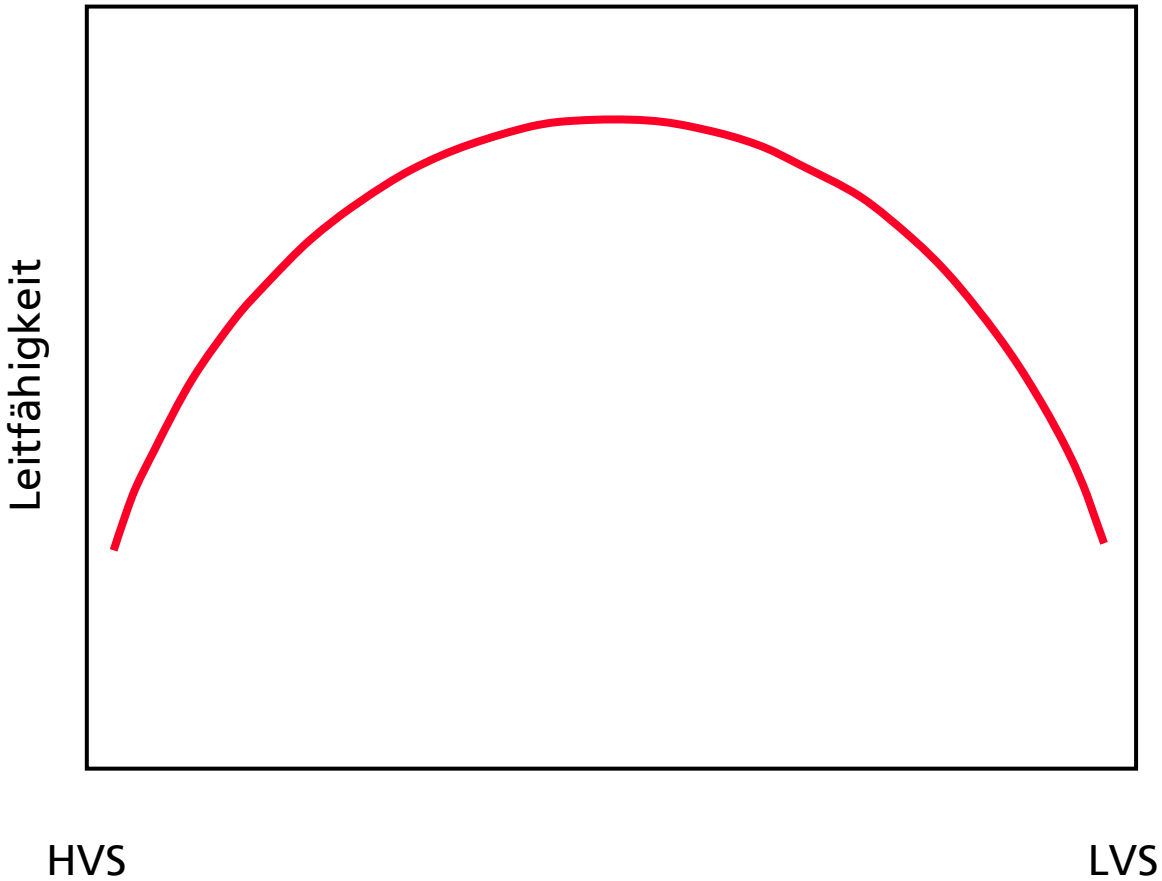
Elektrolyt – Lösemittel

HVS – LVS



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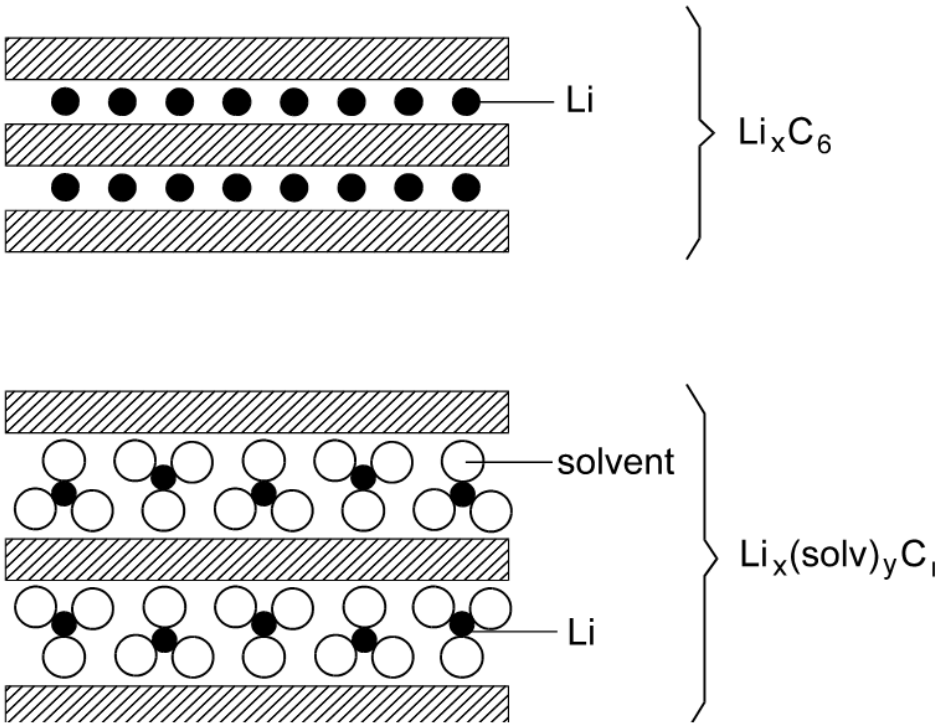
Elektrolyt – Lösemittel

solvatisierte Intercalation mit Propylencarbonat



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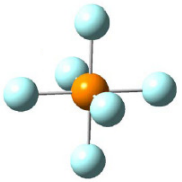
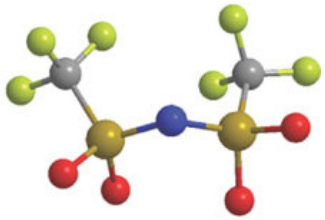
Elektrolyt – Leitsalze

$LiPF_6$

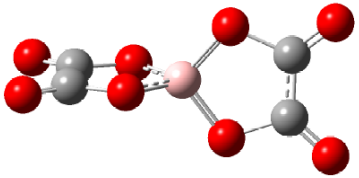


$LiBF_4$

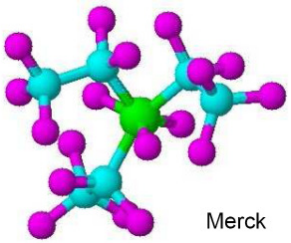
$LiN(SO_2CF_3)_2$ (LiTFSI)



$LiBC_4O_8$ (LiBOB)



$LiPF_3(CF_2CF_3)_3$ (LiFAP)



Merck

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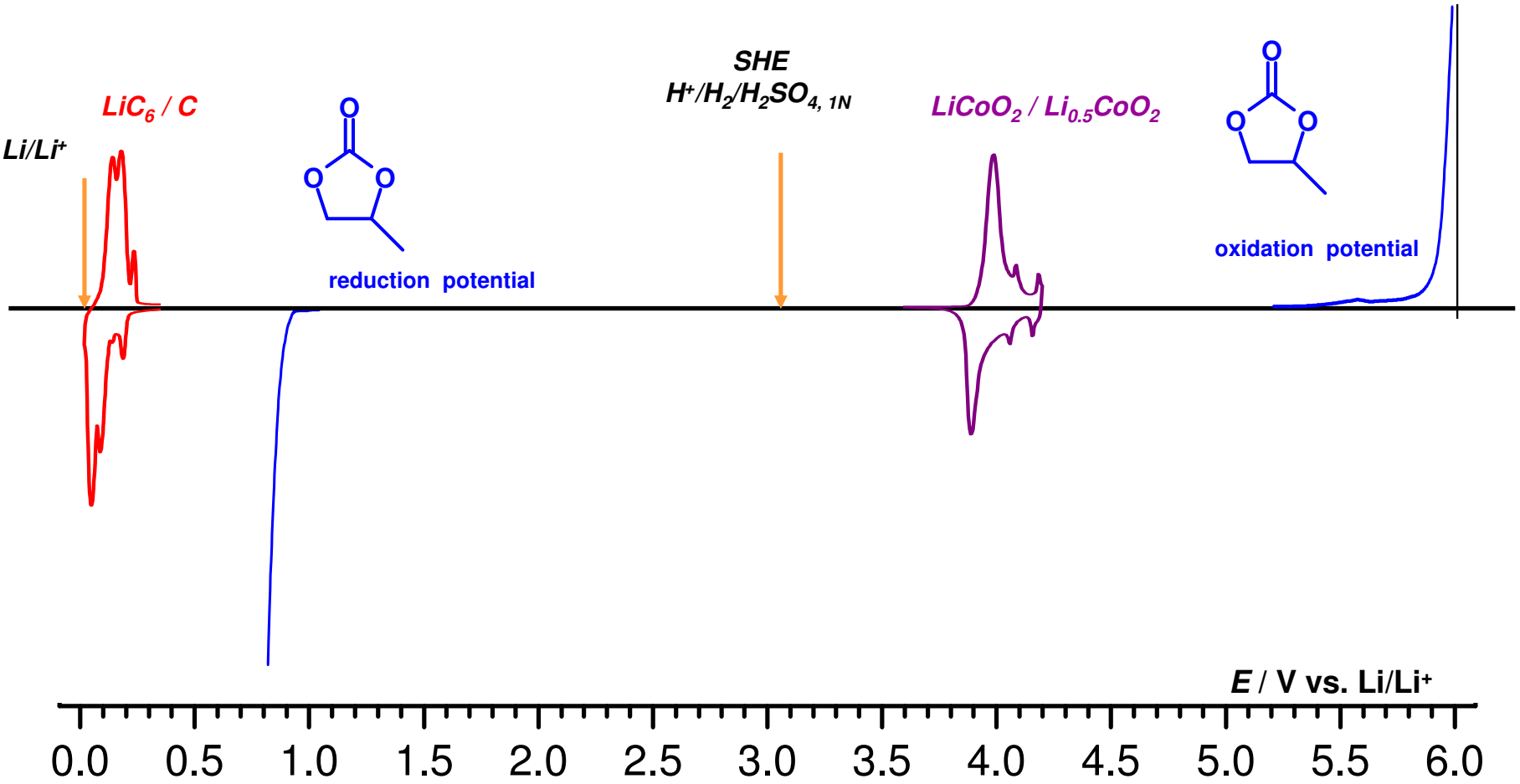
Elektrochemisches Fenster – die Elektrolytstabilität



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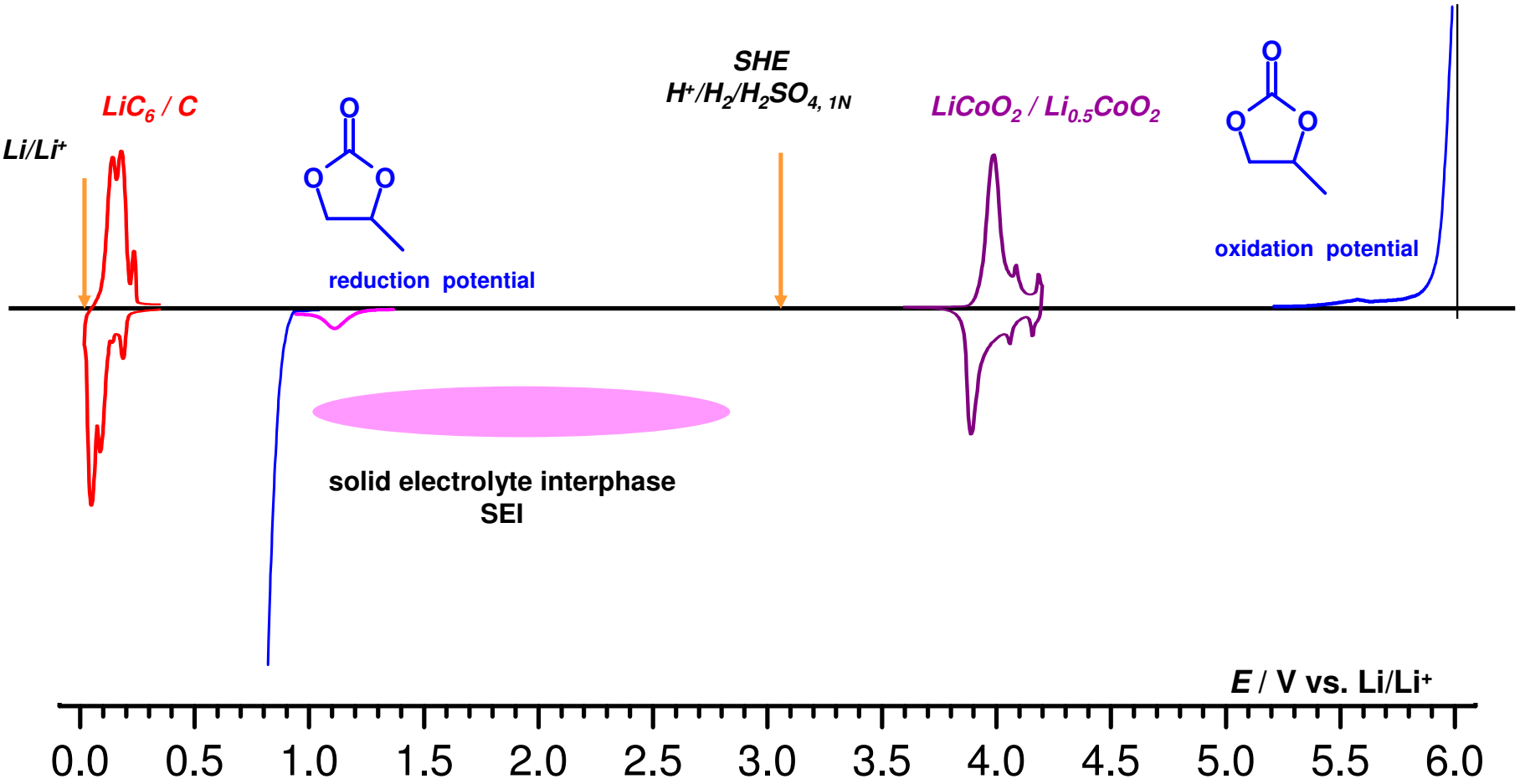
Elektrochemisches Fenster – die Elektrolytstabilität



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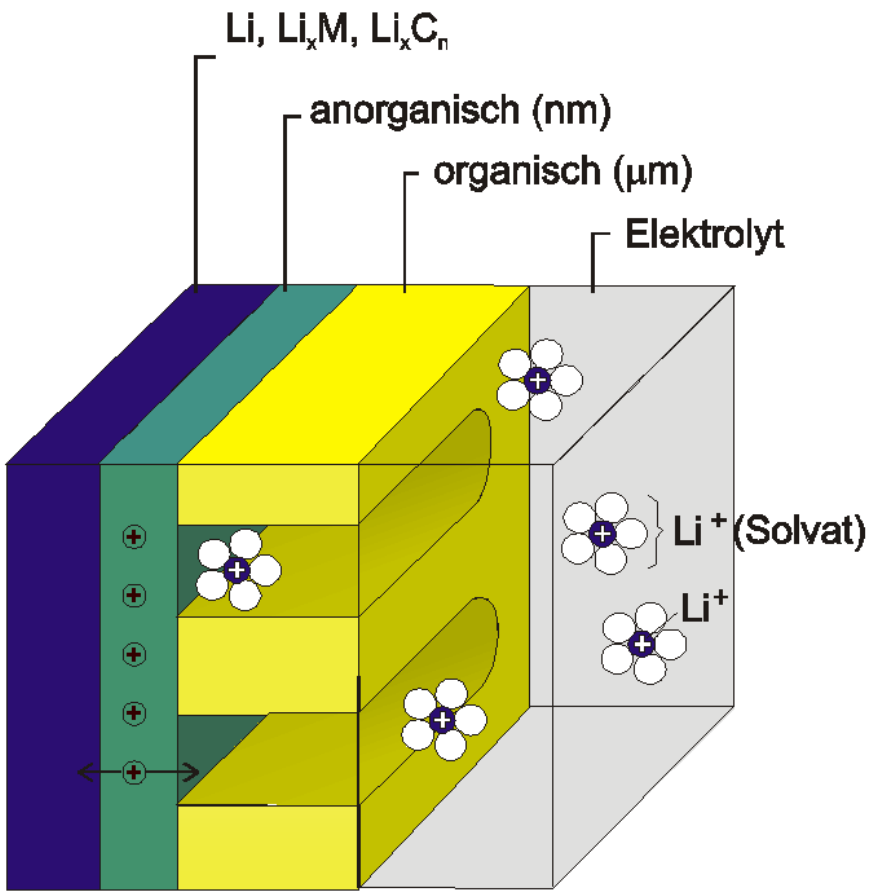
SEI – Solid Electrolyte Interphase



- in situ-Bildung beim ersten Laden
- elektronisch isolierend
- gute ionische Leitfähigkeit für Li^+
- irreversible Reduktion der Elektrolytkomponenten
- geringe irreversible Kapazität (Verbrauch Kathodenmaterial !)
- geringe Gasbildung bei Formierung
- thermisch stabil
- elastisch

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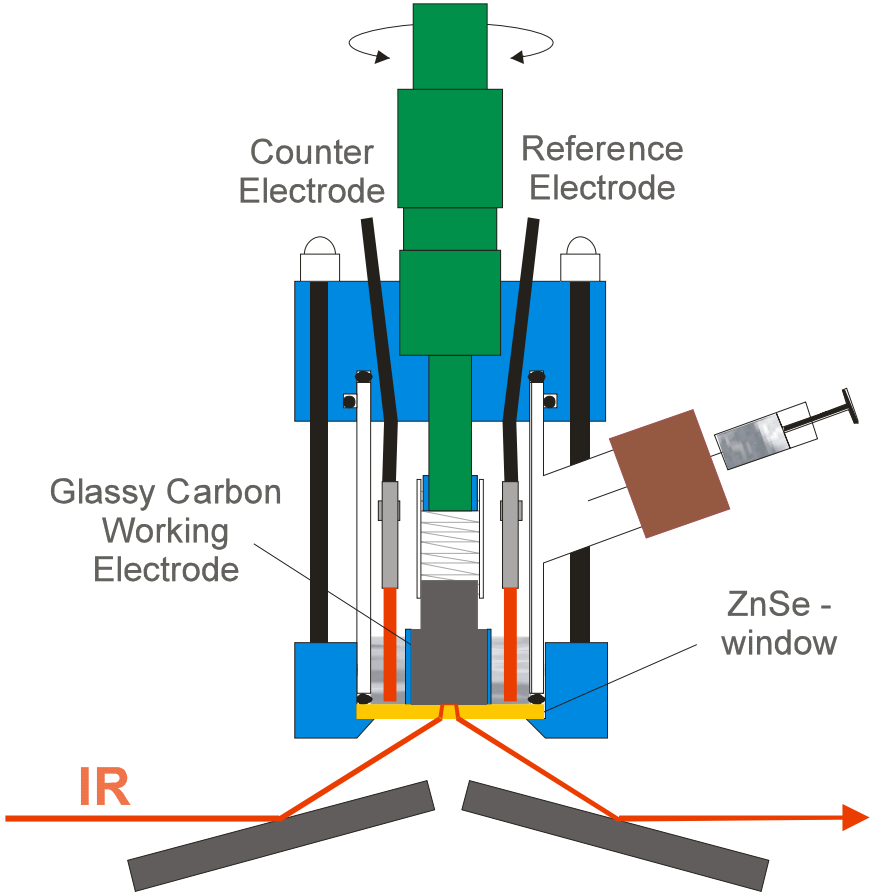
SEI – Solid Electrolyte Interphase

***in situ* IR-Messungen**



Möller, Santner, Kern, Yamaguchi, Besenhard, Winter,
J. Power Sources **2003**, *119-121*, 561-566

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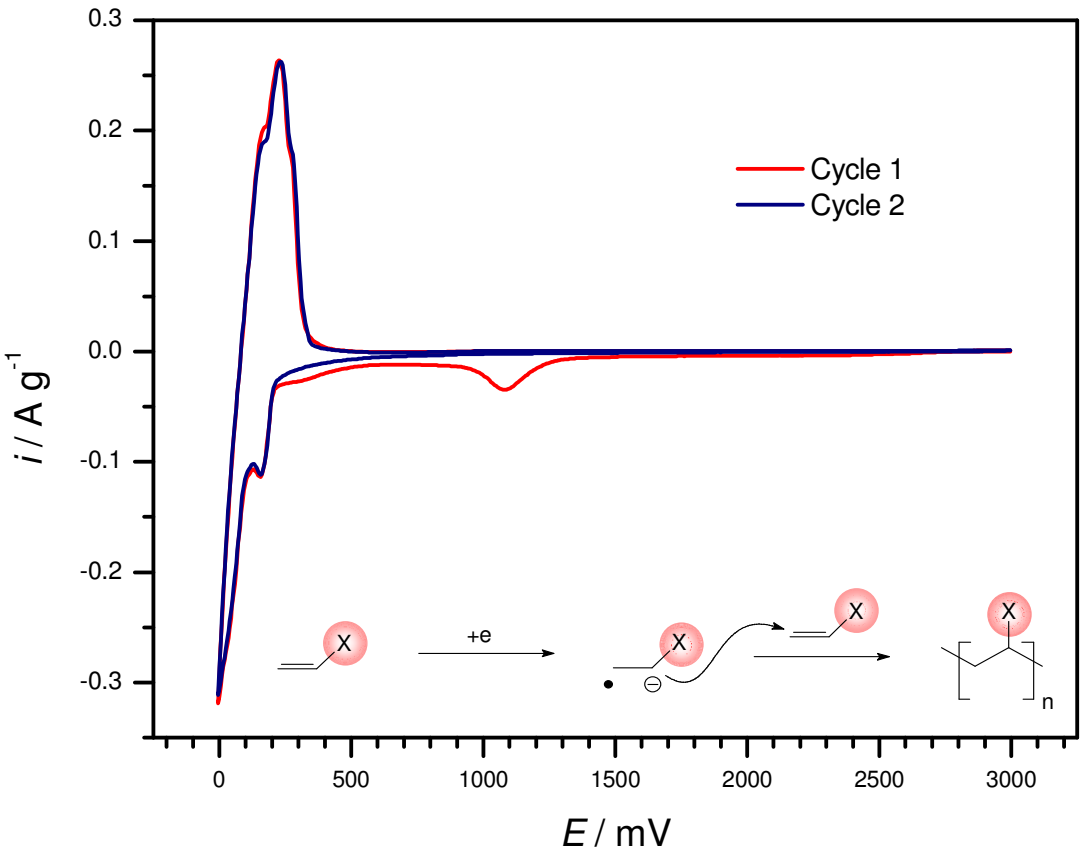
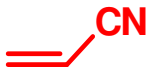
SEI – Solid Electrolyte Interphase





AN

KS 6 Kompositelektrode in 1M $LiClO_4$ + PC / AN (99 : 1), Scanrate 0.05 mV/s

Santner, Möller, Ivančo, Ramsey, Netzer, Yamaguchi, Besenhard, Winter, *J. Power Sources* **2003**, *119-121*, 368-372

Möller, Besenhard, Winter, JP2003086248, **2003**

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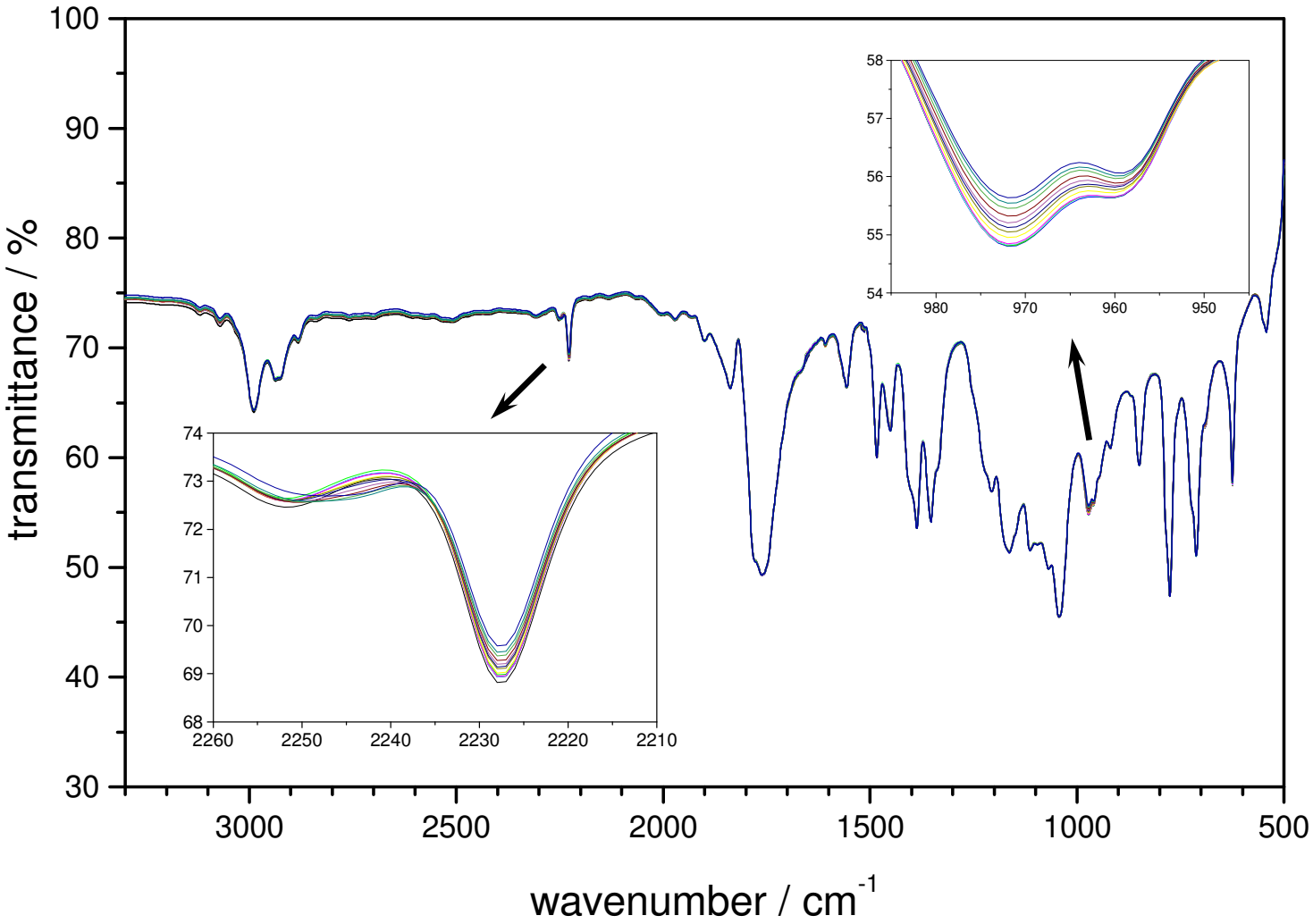
SEI – Solid Electrolyte Interphase



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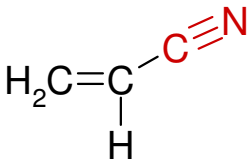
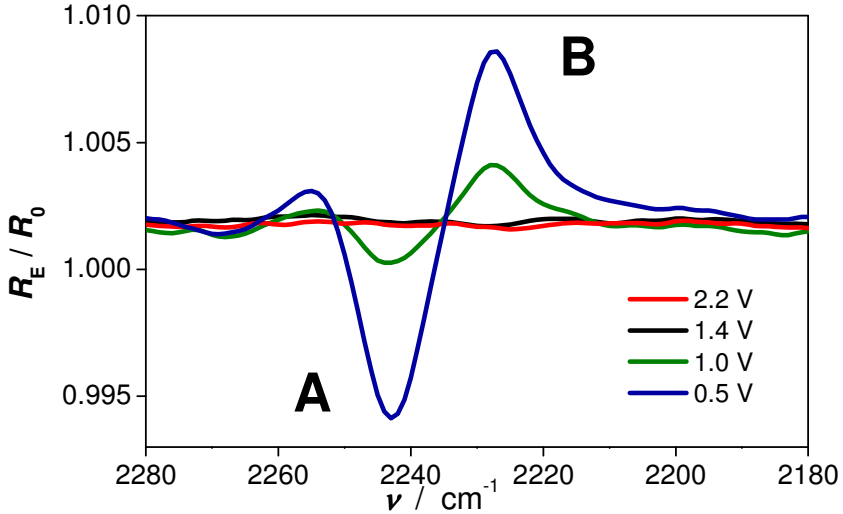
SEI – Solid Electrolyte Interphase

C≡N Streckschwingung

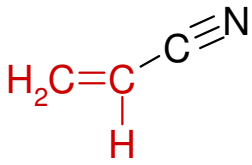


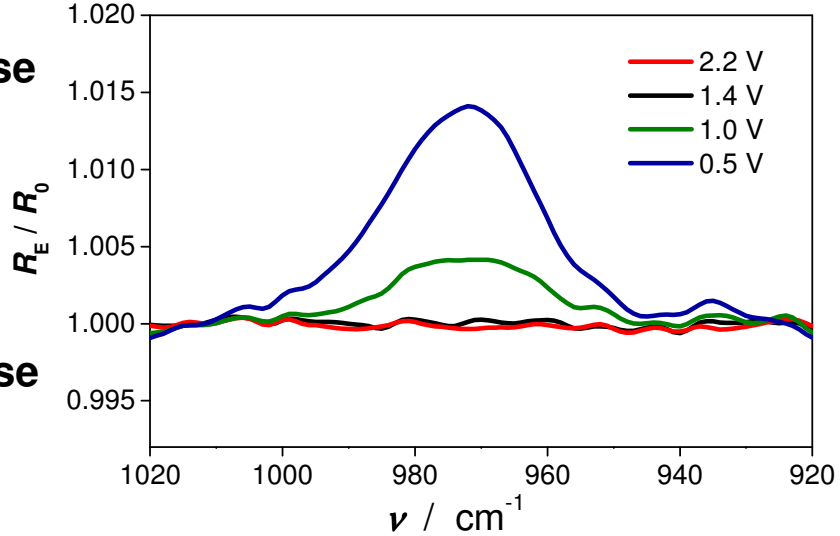


decrease

increase

(HC=CH$_2$) C-H Deformationsschwingung





A ges. Nitril (2245 cm^{-1})

B unges. Nitril (2225 cm^{-1})

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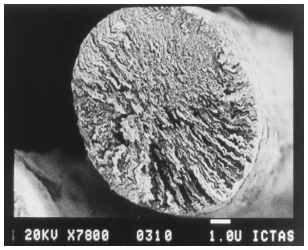
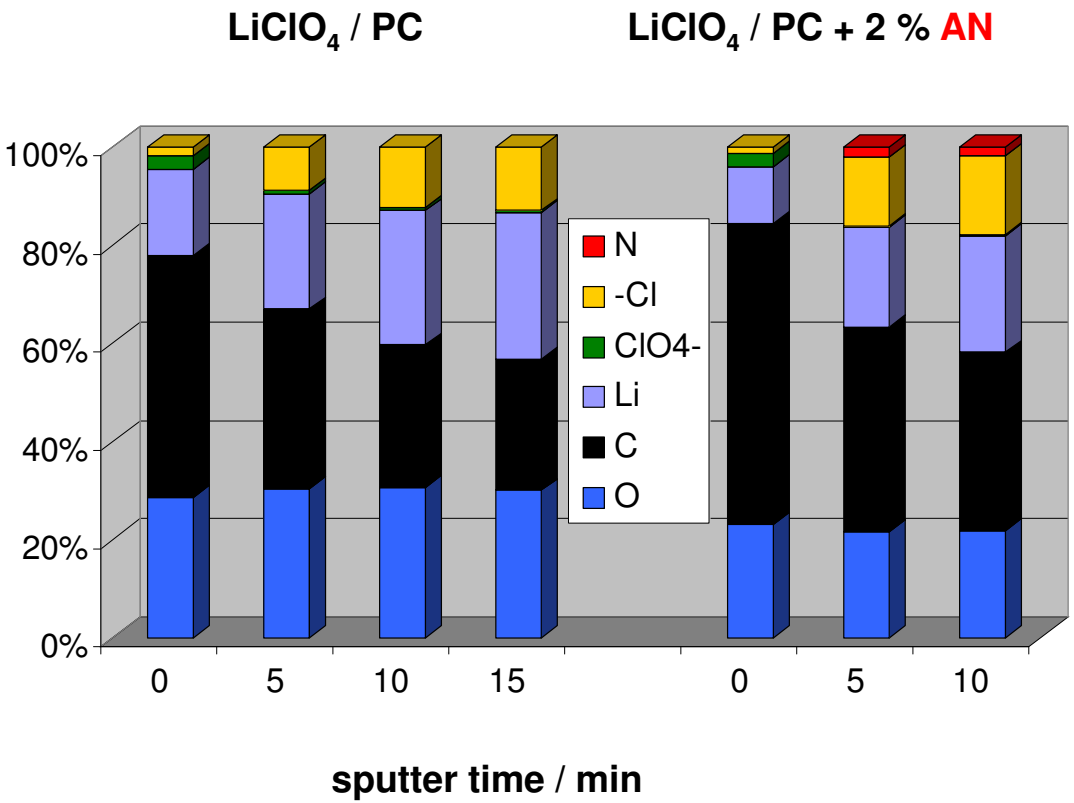
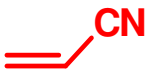
SEI – Solid Electrolyte Interphase

XPS-Analyse



Kohlenstofffaser (meso phase pitch fibres, P100)





AN

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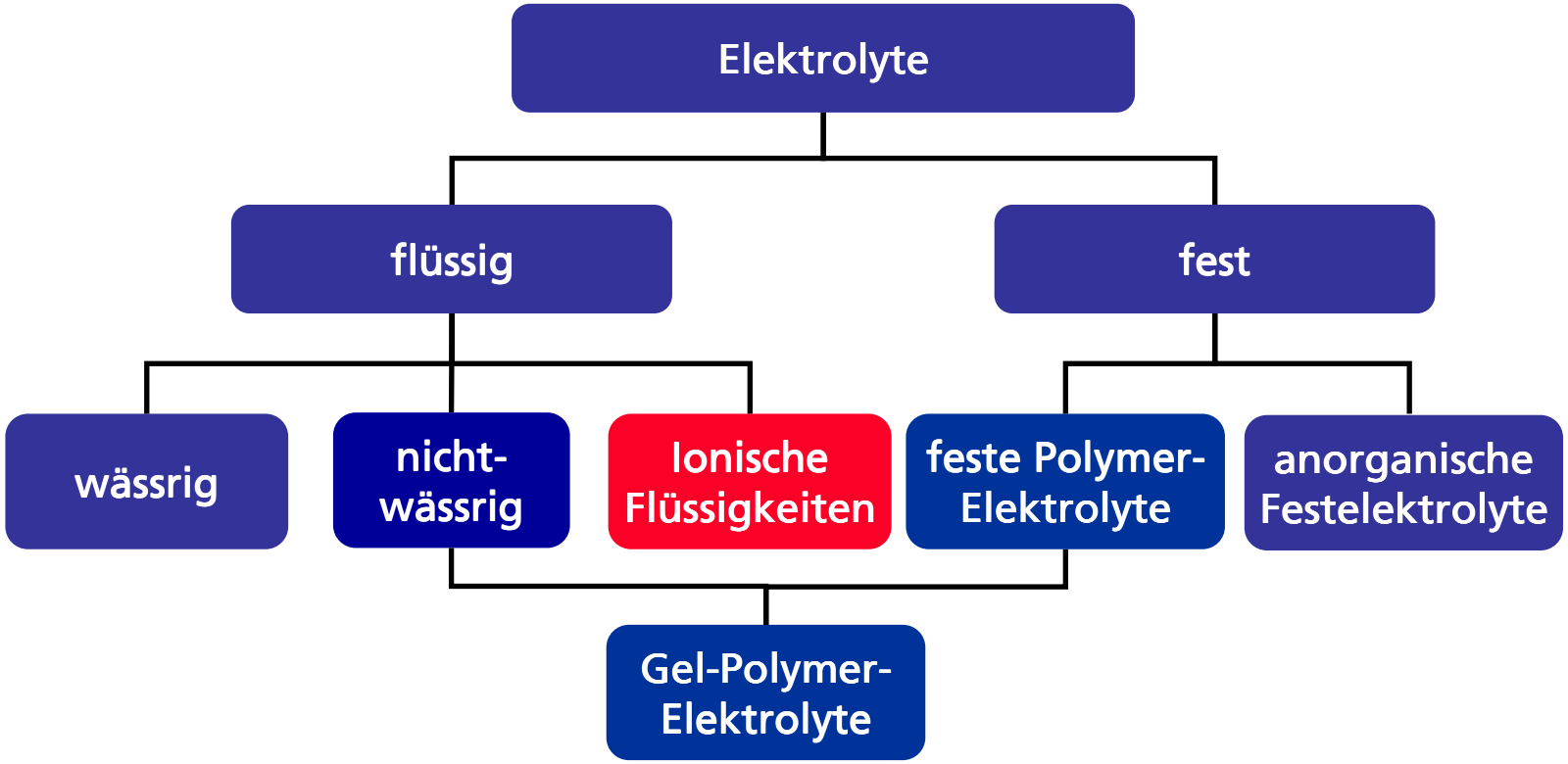
Elektrolyte



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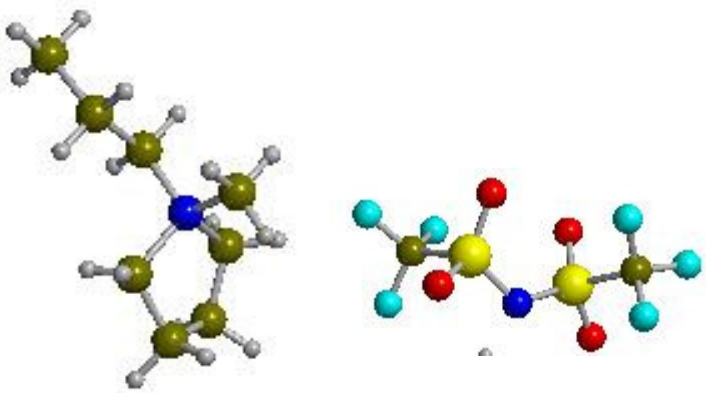
Elektrolyte – Ionische Flüssigkeiten

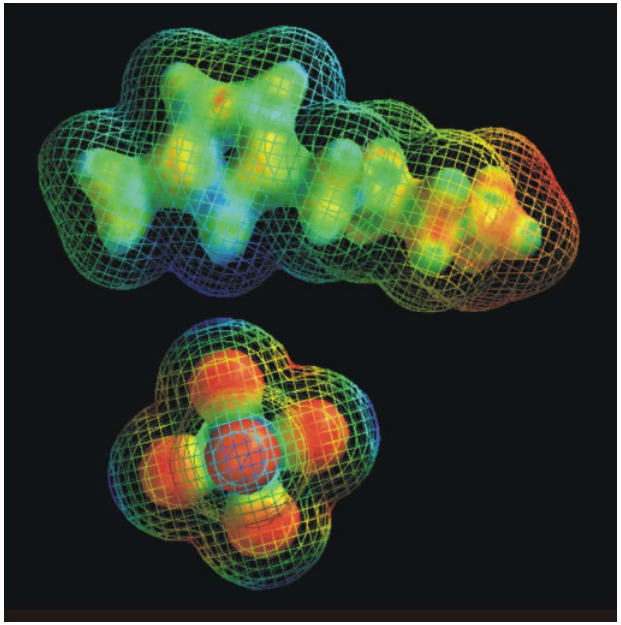
- **großes elektrochemisches Fenster**
- **hohe Temperaturstabilität**
- **wenig entflammbar**

- **schlechtere Tieftemperatureigenschaften**
- **Preis und Verfügbarkeit**



Pyrrolidinium-Salze

„Benchmark IL für Lithiumzyklisierung“



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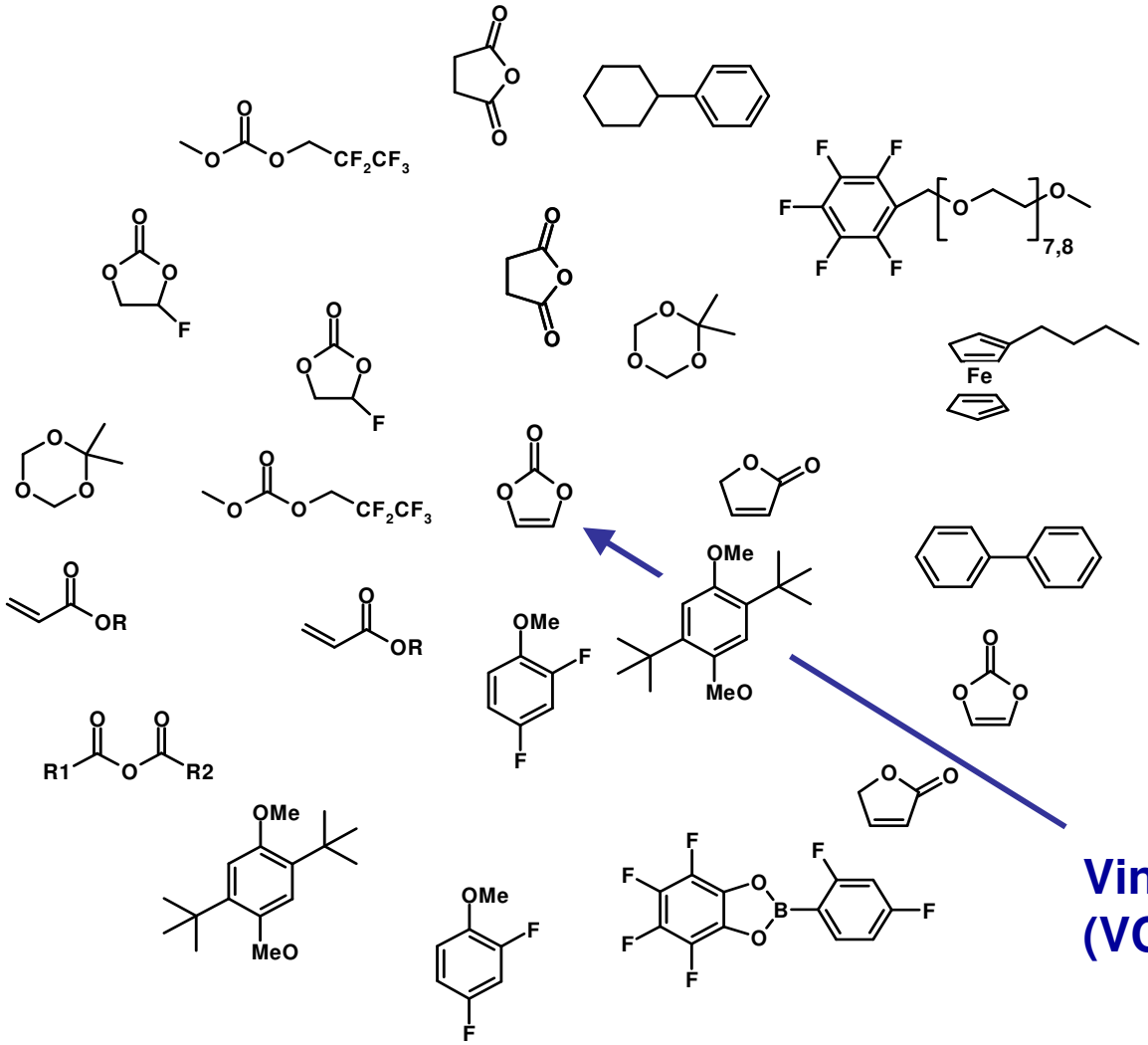
Elektrolytadditive



Vinylencarbonat (VC)

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Elektrolytadditive

- **Additive zur verbesserten SEI-Bildung**
- **Tieftemperaturadditive**
- **Flammhemmende Additive**
- **Benetzungsadditive**
- **Anionenrezeptoren:** Erhöhung der Li-Diffusion und der Transportzahl, thermische Stabilisierung
- **Additive für glatte Li-Abscheidung**
- **Wasser-/Säurefänger**
- **Überladeadditive**

  Redox-Shuttle

  Gasbildende Additive zur Aktivierung eines CID (current interrupter device)

  polymerisierende Additive (shut-down, leitfähig)

Functional Electrolyte

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Lithium-Ionen-Batterie

5033 × 18650

42 g

5033 Zellen
214 kg

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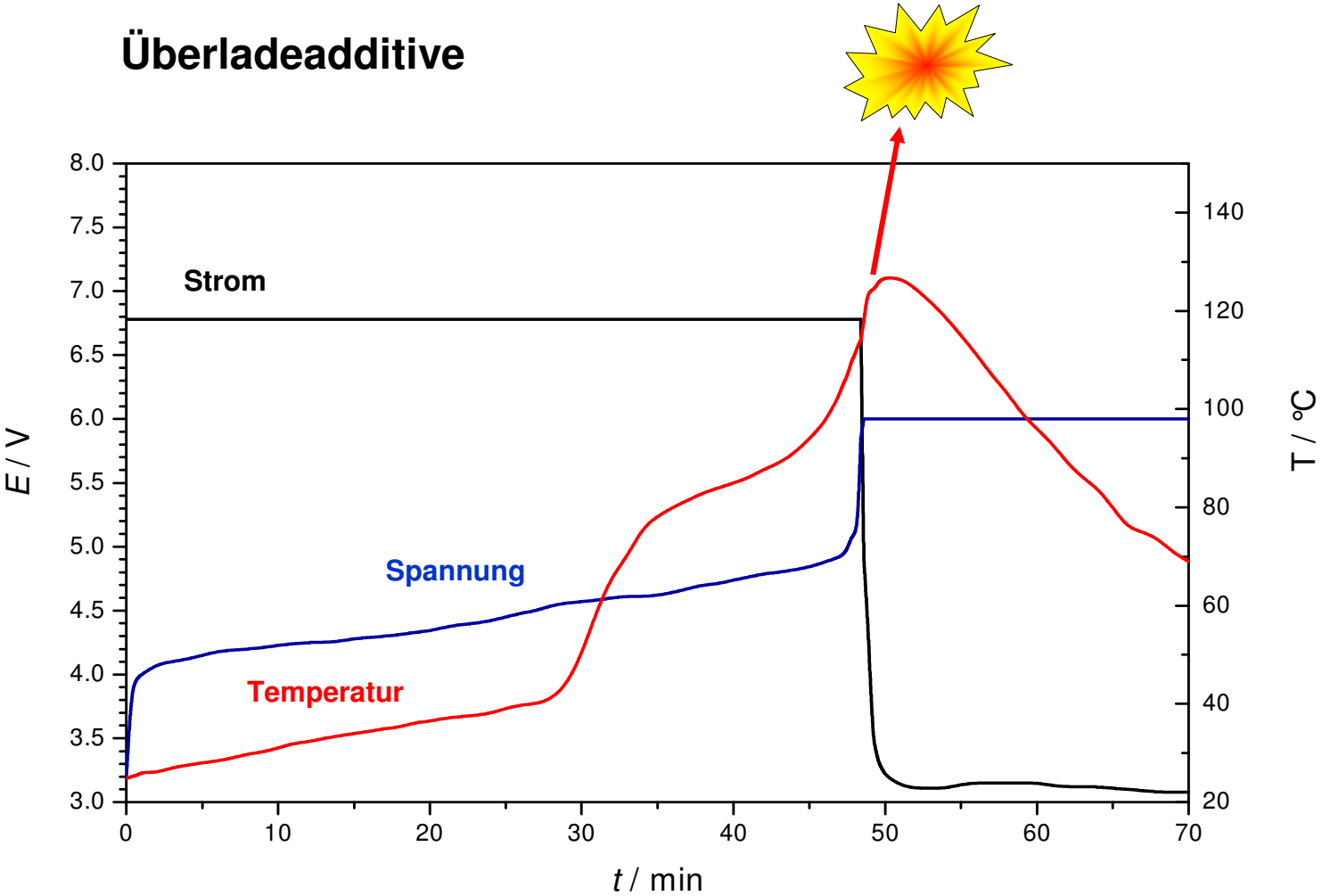
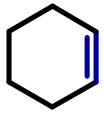
Überladeadditive





Überladetest mit Konstantstrom (2C-Rate), danach Konstantspannung (6 V)

Möller, Fauler, Winter, Besenhard, Applicant: LG Chem., US Patent 6,942,949, **2005**.

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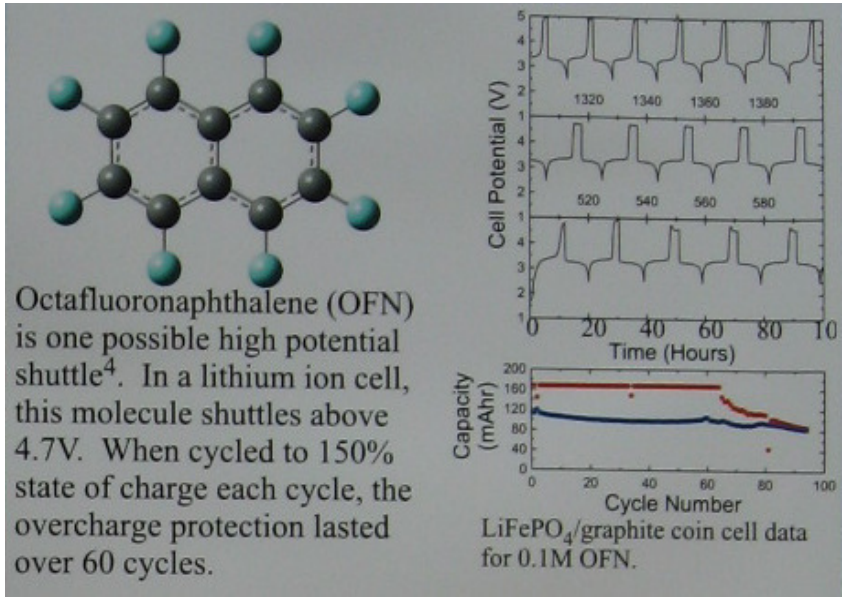
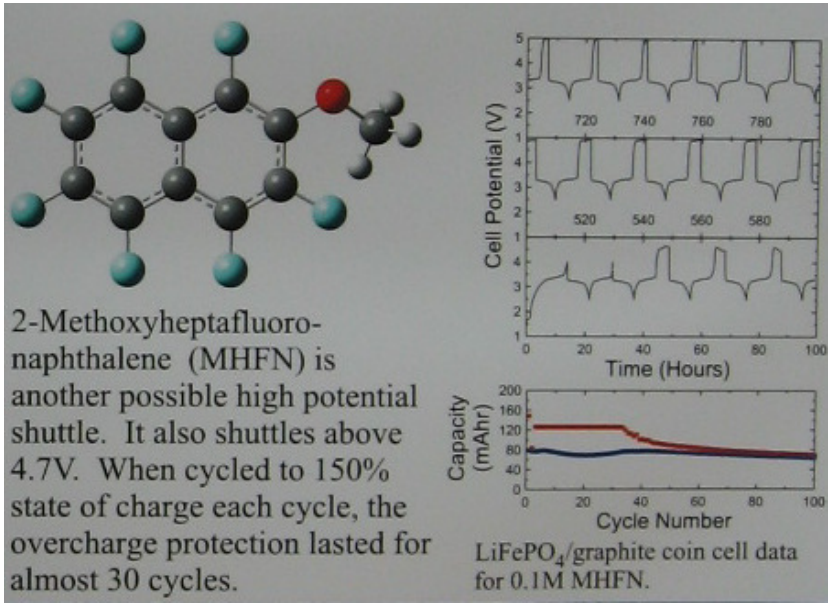
Überladeadditive

Redox-Shuttles





Jeff Dahn et al.

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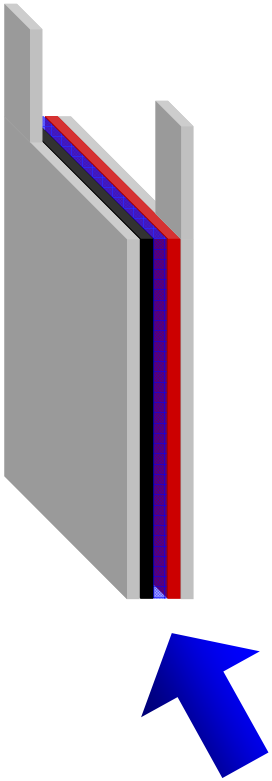
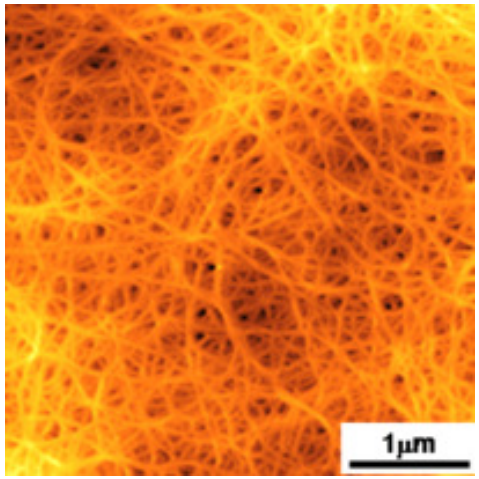
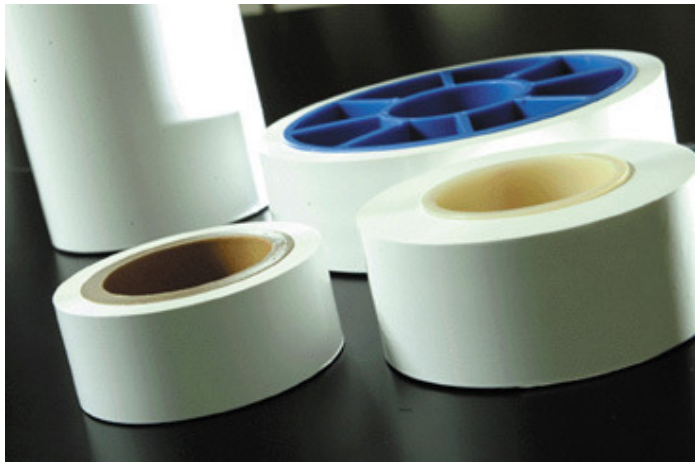
Separatoren: Mikroporöse Olefinmembranen

Interaktionen des Elektrolyten mit den Elektroden (Binder) und dem Separator



- Benetzung
- Quellung





TonenGeneral Sekiyu K.K.

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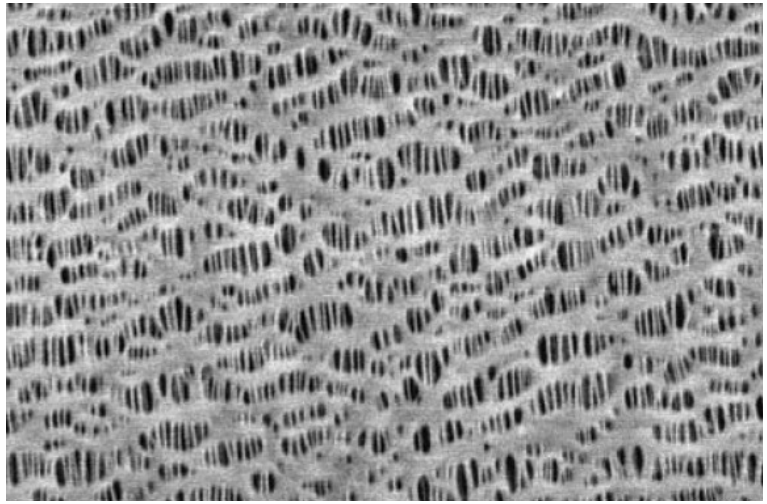
Separatoren: Mikroporöse Olefinmembranen



Celgard 2340: PP/PE/PP

Properties	Unit	Typical Value
Porosity	%	45
Pore Size	µ x µ	0.038 x 0.90
Gurley	seconds	31
Thickness	µ	38
Shrinkage	%	5
Tensile Strength, MD	kg/cm^2	2100
Tensile Strength, TD	kg/cm^2	130
Melt Temperature	°C	135 / 163
Adhesion / Peel Strength	gms/in	> 15

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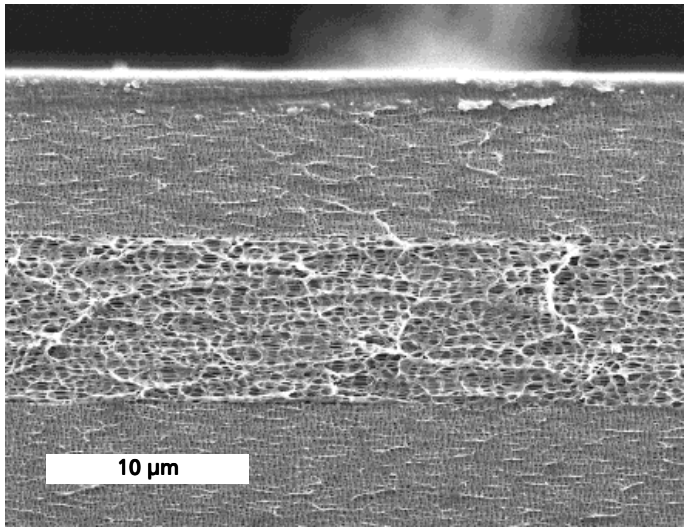
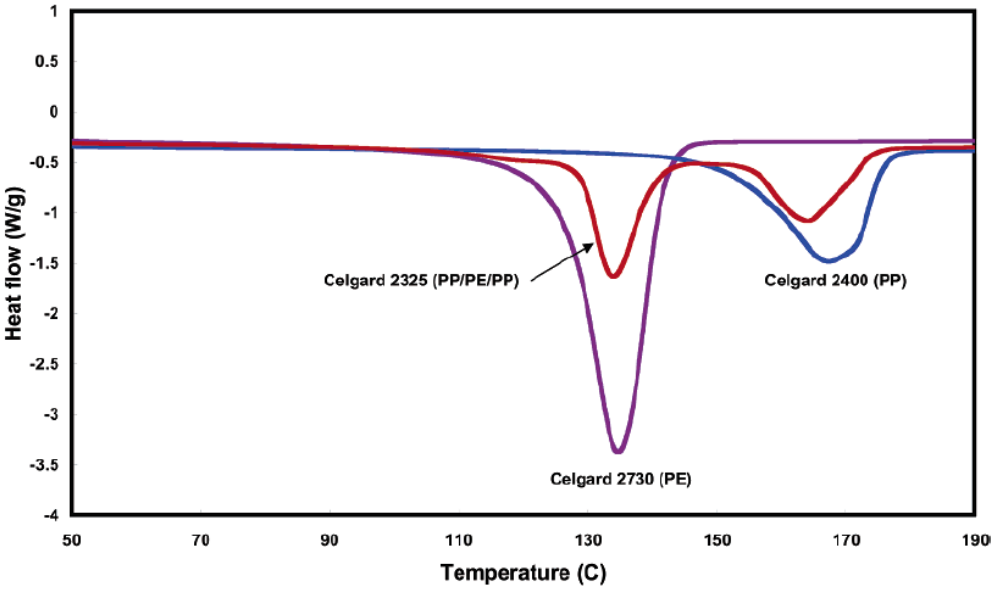
Separatoren: Mikroporöse Olefinmembranen





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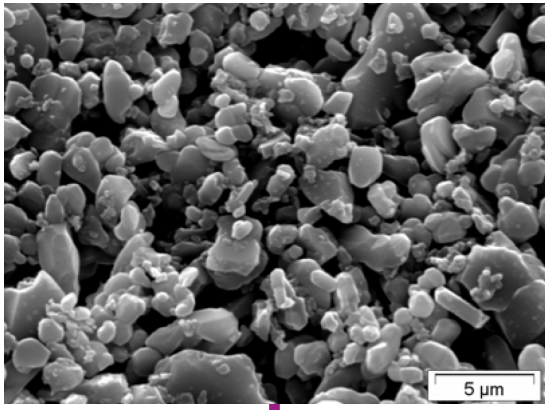
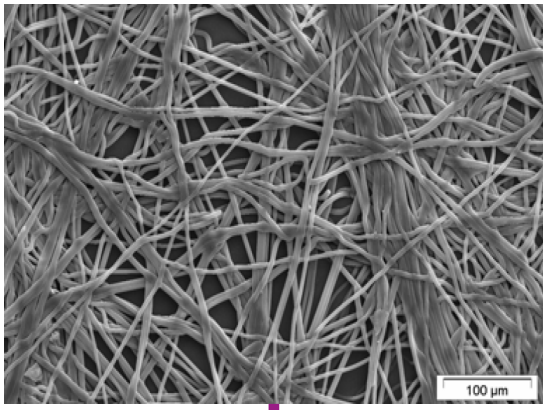
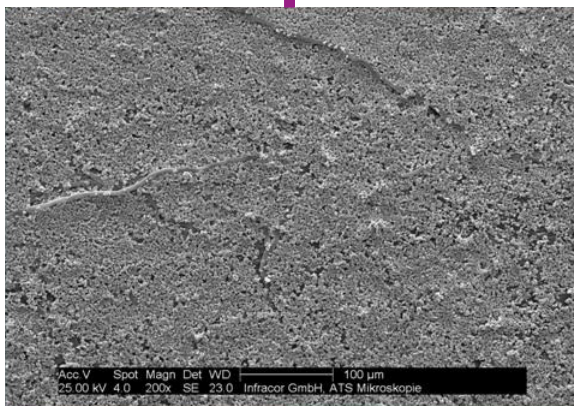
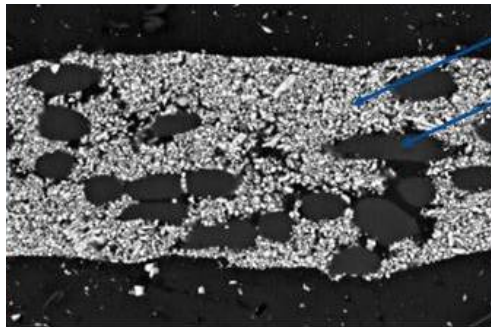
Separatoren: keramischer Separator









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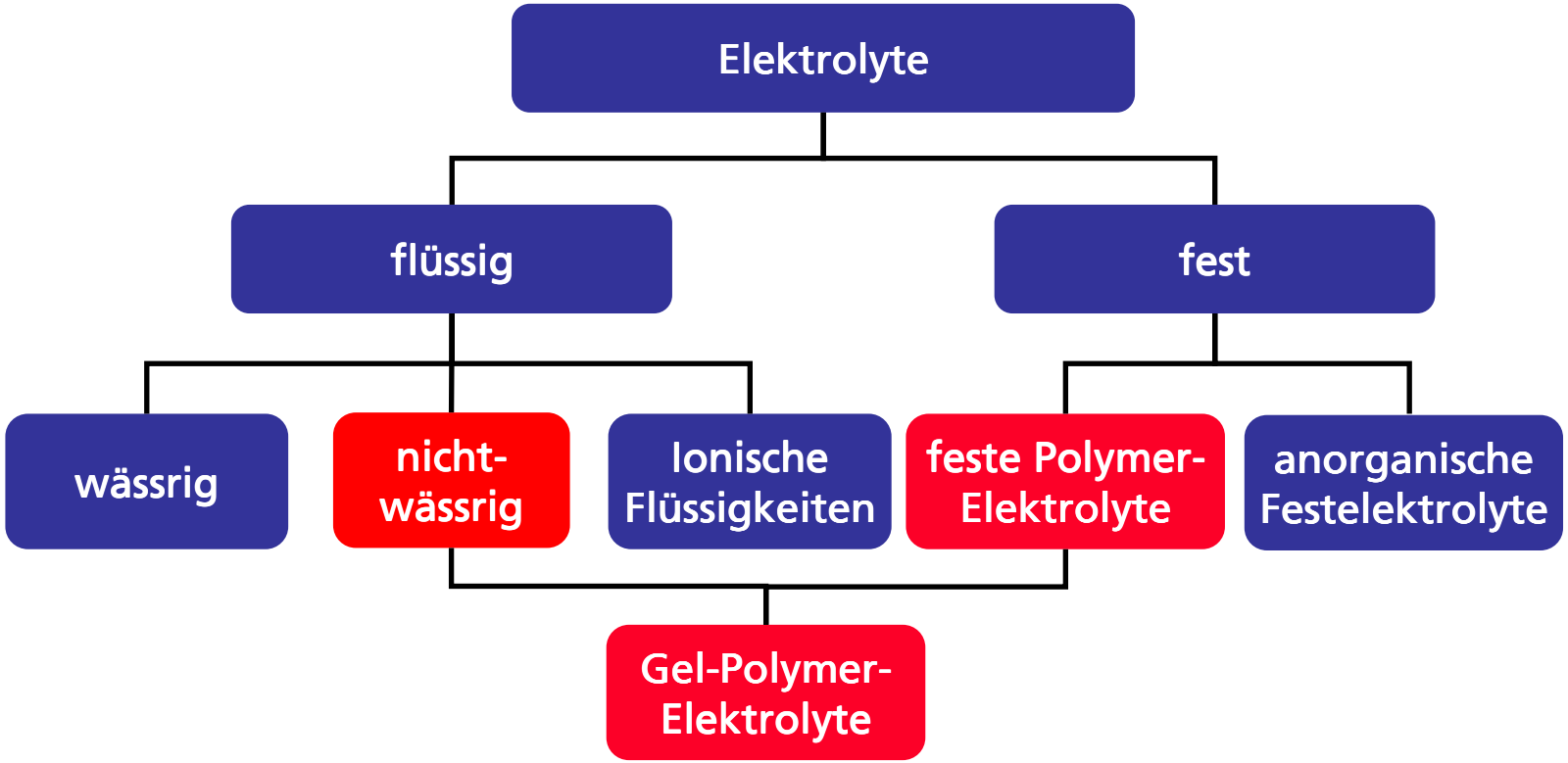
Elektrolyte



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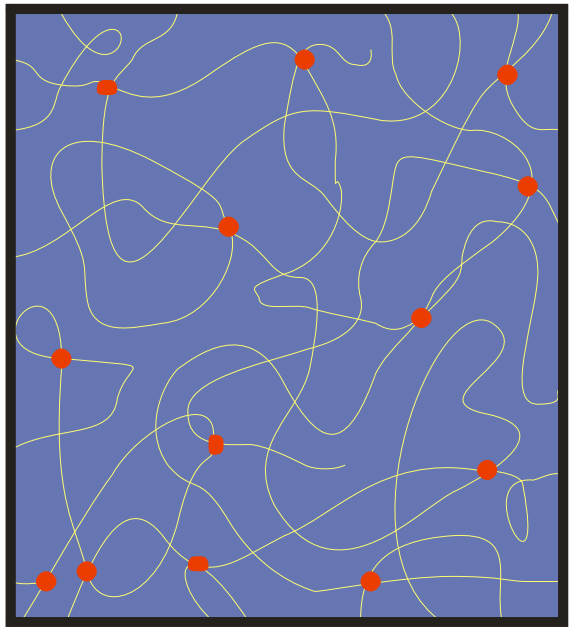
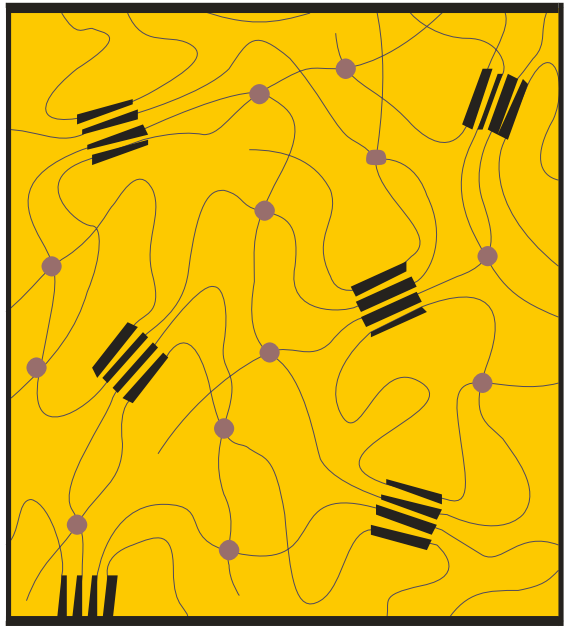
Polymer- und Polymer-Gel-Elektrolyte

trockener Polymerelektrolyt



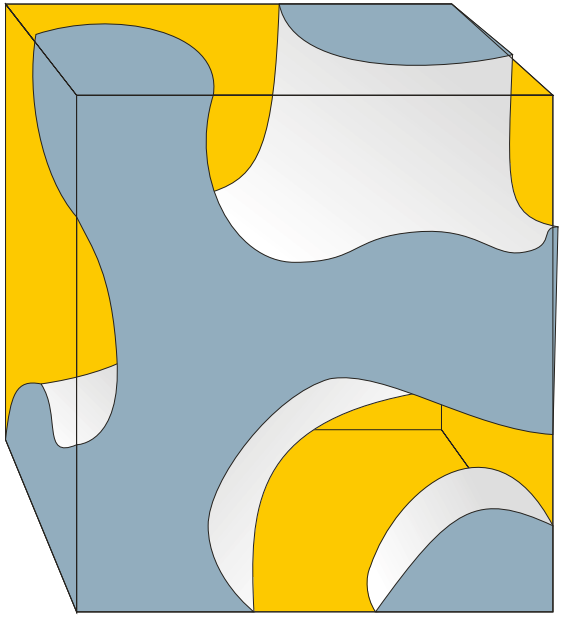
PEO + Li salt

Gel-Polymer-Elektrolyt



PVdF-HFP, geliert mit flüssigem Elektrolyt

flüssiger Elektrolyt + Separator



mikroporöser Separator (PE, PP), getränkt mit flüssigem Elektrolyt

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Lithium-Polymer-Zellen

prismatisch (Flachzelle)

Edelstahl-/
Aluminiumbehälter

Aluminium-
Verbundfolie

zylindrisch (Rundzelle „18650“)

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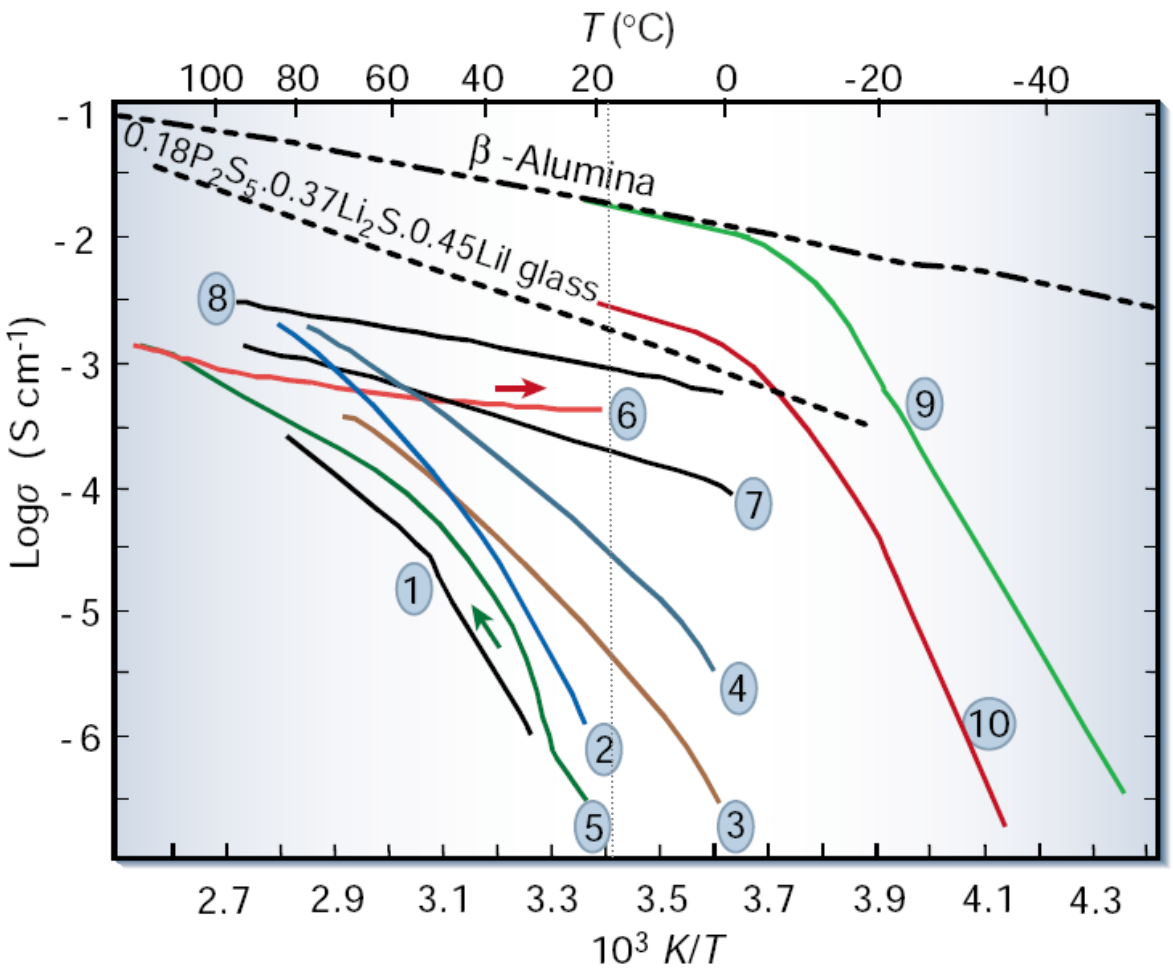
Leitfähigkeiten ausgesuchter Li-Elektrolyte



1: First generation PEO-$LiCF_3SO_3$

2: new solutes with high-dissociation PEO-$Li[(CF_3SO_2)_2N]$

3: low-T_g combination polymer

4: plasticized polymer electrolyte PEO-$Li[(CF_3SO_2)_2N]$ & 25% w/w PEG-dimethylether (mw 250)

7: gel-type polymer (X-linked PEO-dimethacrylate-$Li[(CF_3SO_2)_2N]$-PC 70%)

8: liquid electrolyte PC/DME $LiCF_3SO_3$

9: liquid electrolyte EC/DMC-$LiPF_6$

10: gel electrolyte P(VDF-HFP)/EC/DMC-$LiPF_6$

J.-M. Tarascon, M. Armand, Nature 2001, 414, 359

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SONYs „Advanced Polymer Electrolyte Lithium-Ion Cell“

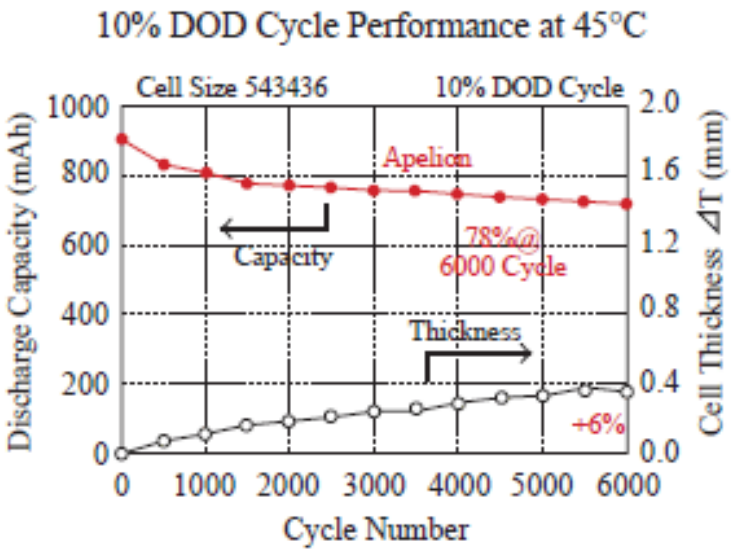
Fluoropolymer mit carbonat-basiertem Elektrolyten mit $LiPF_6$

Apelion *by* SONY

- höhere Leistungsdichte
  verbesserte Leitfähigkeit: 3. 5 → 9 mS/cm

- höhere Energiedichte (241 Wh/kg !)
  verbesserte Stabilität an der Kathode: 4.2 → 4.4 V

- verlängerte Haltbarkeit (Zyklus 500: (85 % Restkapazität)
  verbesserte Haftung zwischen Anode und Separator: 0.4 → 0.7 N/cm
  verringerte Zellschwellung: +10 % → +4 % (500 Zyklen)



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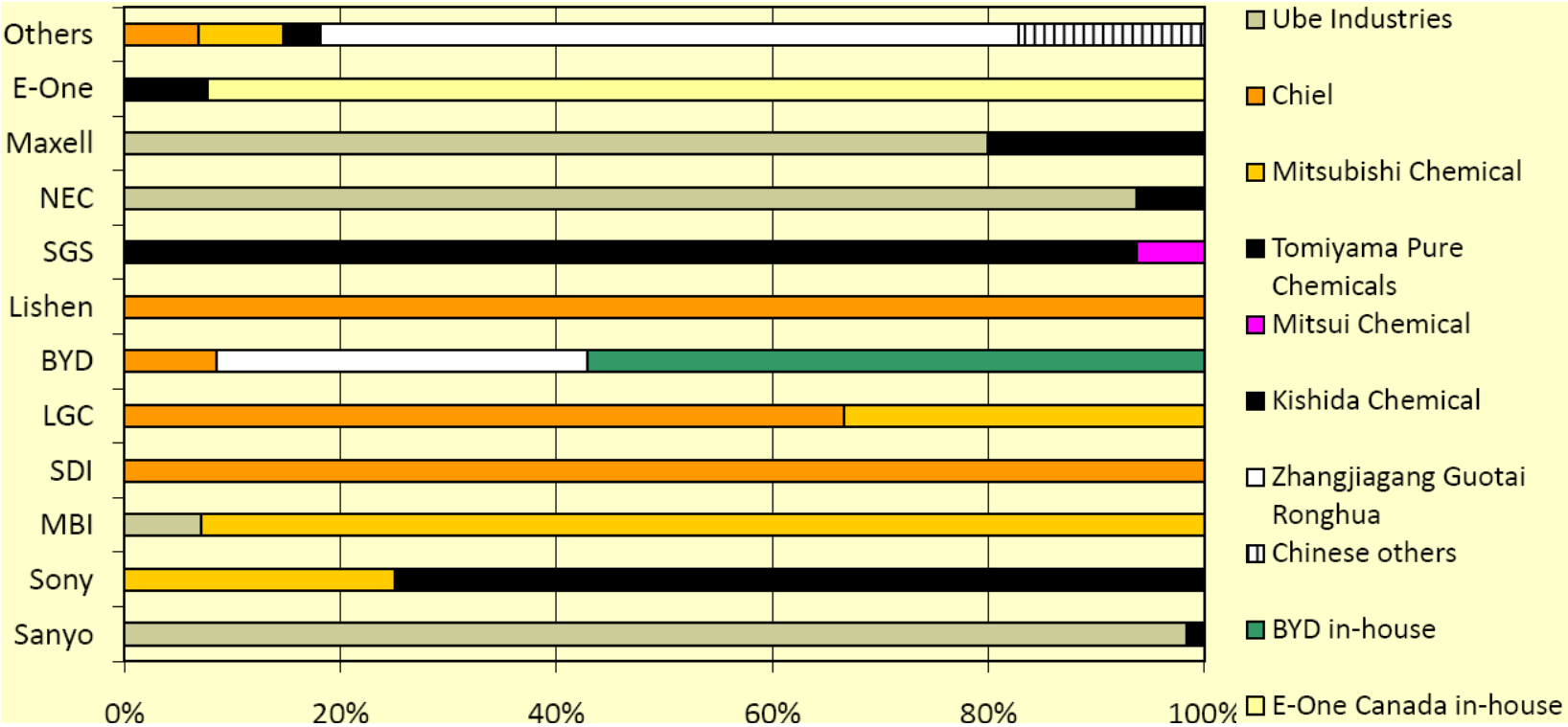
Elektrolytmarkt für Lithium-Ionen-Batterien



The rechargeable battery market, 2007-2020, JUNE 2009 (Avicenne Développement)

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© ZAHA HADID ARCHITECTS

Herzlichen Dank!

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