



Elektrolyte für Li-Ion Batterien

Von der Einzelkomponente zum kundenspezifischen Elektrolyten

Materials Valley: Workshop Elektrochemische Energiespeicher und Wandlersysteme

Februar 2010

Outline

- Lithium Ion Battery Environment for Automotive Application
- Requirements for next generation Electrolytes
- Actual R&D topics at Merck
- Electrolyte Optimization
 - Application test
 - Quality

Mobile Energy- Back to Electricity



1900 Porsche Lohner Hybrid

- Voltage: 80V (44 Cells)
- Speed 45-58 km/h

Lead-Acid Battery



1994 Toyota Prius

- Voltage: 200V
- Power: 60 kW
- Energy 1,3kWh
- Weight: 39 kg

Ni MH Battery



2009 Mercedes S400h

- Voltage: 120V
- Power: 15 kW
- Energy 0,7kWh
- Weight: 25 kg

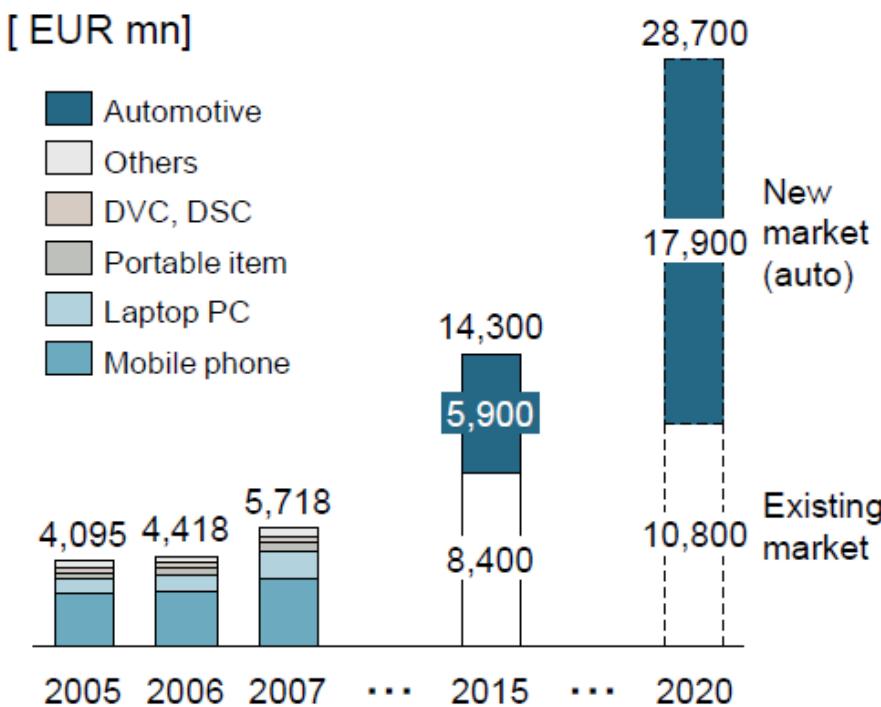
Li-Ion Battery

Lithium Ion Battery Market

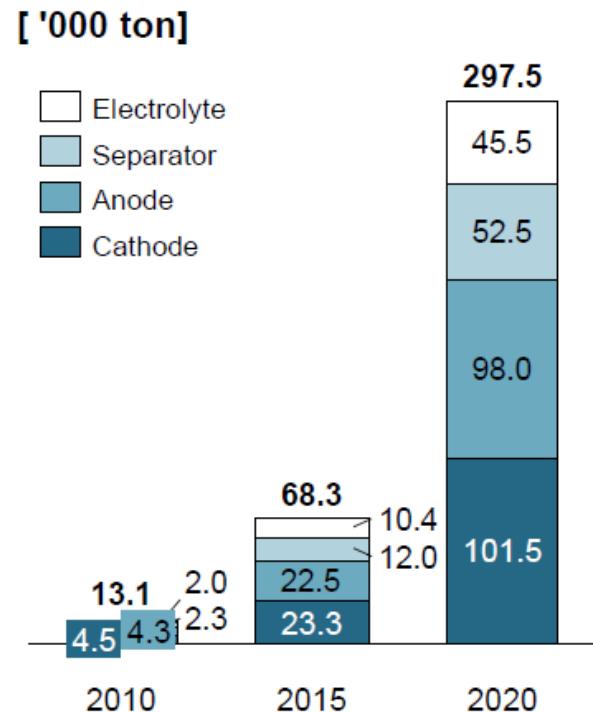
Overview



Market volume by application (Global)



Component market for automotive



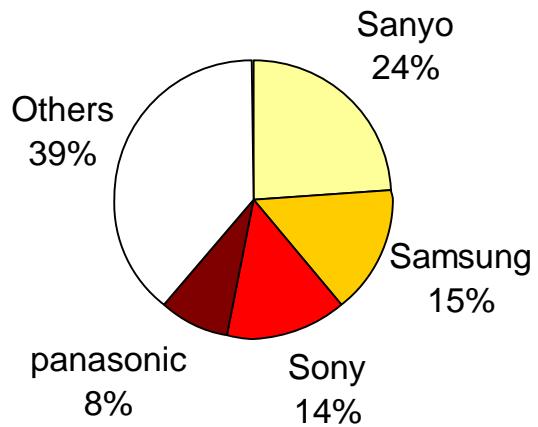
Only automotive shows strong growth potential among applications for LiB

Lithium Ion Battery Market

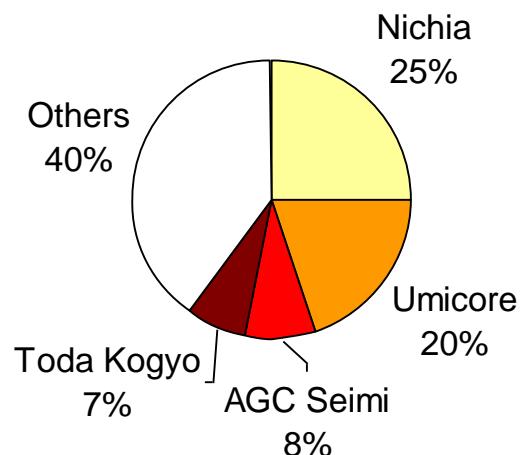
Competition



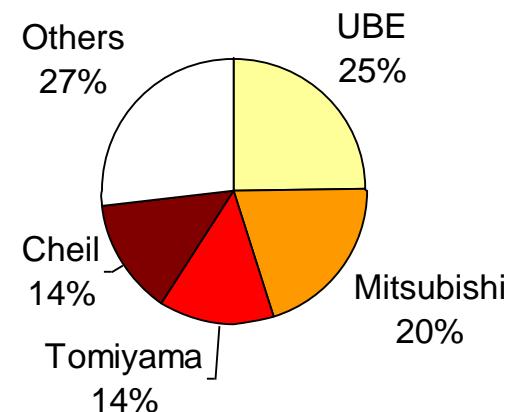
LiB Supplier



Cathode Suppliers

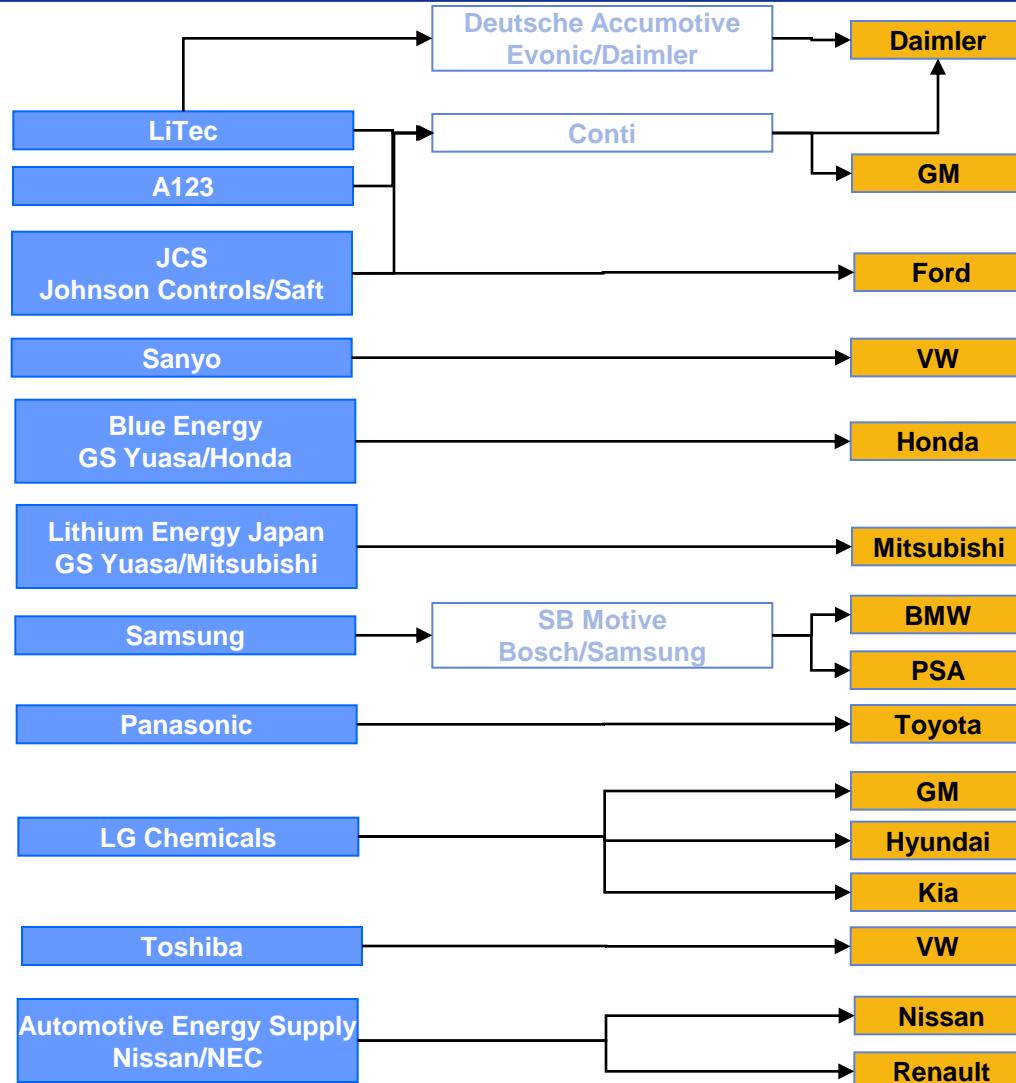


Electrolyte Suppliers



Lithium Ion Battery Market

Overview of selected consortia



Li-Ion Battery

Technology Roadmap

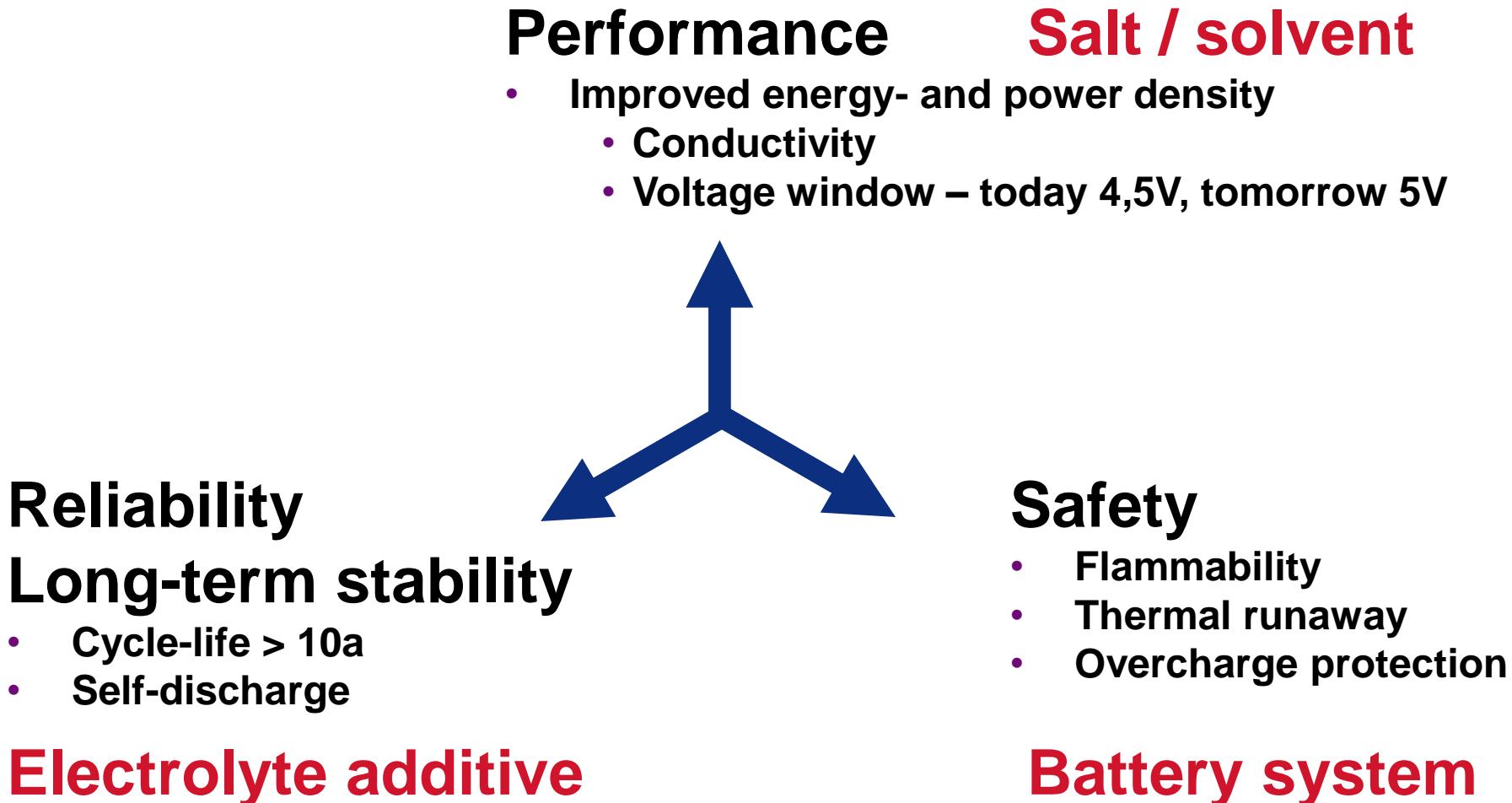


	Today	2010	2015	2020	2030
Battery	Energy density	100Wh/kg	100Wh/kg	150Wh/kg	250Wh/kg
	Power density	400W/kg	1,000W/kg	1,200W/kg	1,500W/kg
	Cost	200,000/kWh	100,000/kWh	30,000/kWh	20,000/kWh
High-power Type(for HEV)	Energy density	70Wh/kg	70Wh/kg	100Wh/kg	200Wh/kg
	Power density	1,800W/kg	2,000W/kg	2,000W/kg	2,500W/kg
	Cost [JPY]	200,000/kWh	100,000/kWh	30,000/kWh	20,000/kWh
component	Cathode	Spinel	$\text{Li}_2\text{MO}_3\text{-LiMO}_2$	$\text{Li}_2\text{MPO}_4\text{F}$	Innovative next-generation battery
	Electrolyte	LiPF_6 / carbonates	LiPF_6 / carbonates	Ionic liquid	
	Anode	Carbon/graphite	Carbon/graphite	Alloy	

Source: New Energy and Industrial Technology Development Organization, NEDO

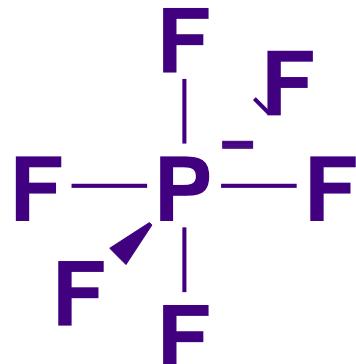
100 JPY = 0,8 Euro

Requirements for next generation Electrolytes



LiPF₆ based electrolytes

Still the dominating system



Highly conductive:
Electrochem. stable:

> 10mS/cm @ RT in EC:DMC 1:1
> 4,8 V vs. Li/Li⁺

Sensitive towards hydrolysis
Limited thermal stability

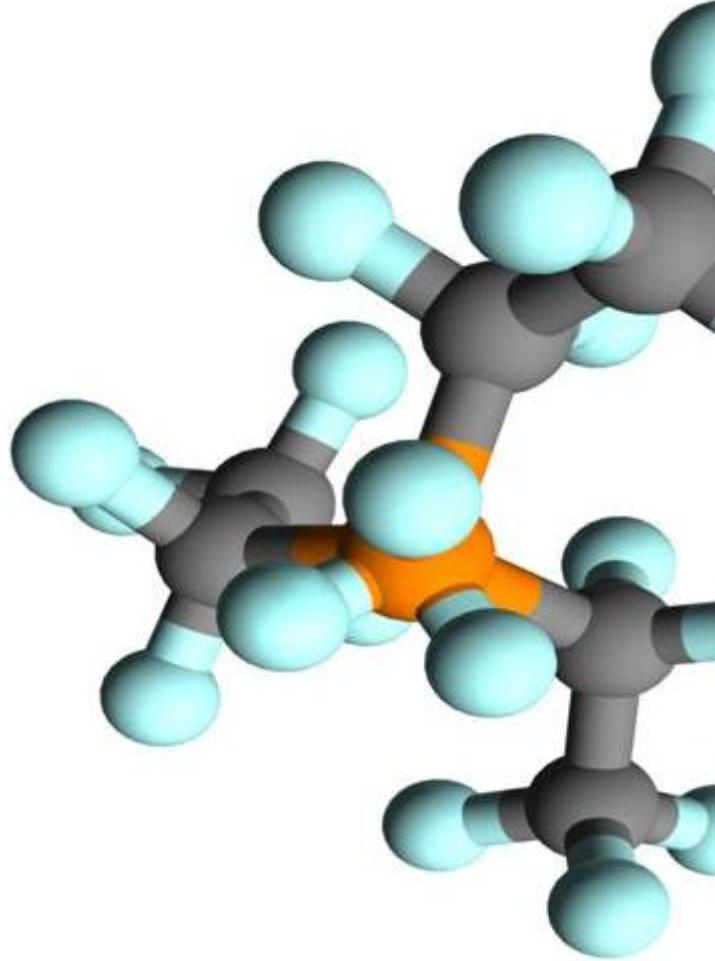
	EC	PC	DMC	DEC	EMC
MP/°C	36,4	-48,8	4,6	-74	-53
BP/°C	248	242	91	126	110
η/cP	1,9 (40°C)	2,53	0,59	0,75	0,65
ϵ	89,8	64,9	3,1	2,8	2,9

Electrolyte R&D

Major Topics at Merck



- **Safety, high temperature**
 - Thermally and hydrolytically stable conducting salts
- **Power density, low temperature**
 - Electrochemically stable additives to improve wetting of electrodes and separator



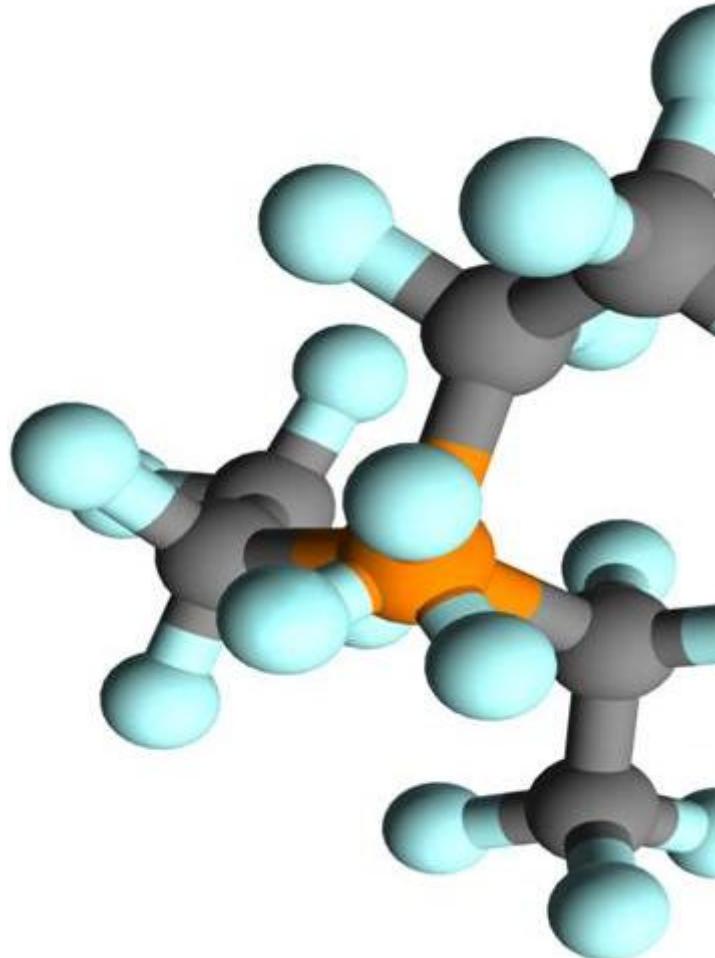
Electrolyte R&D

Major Topics at Merck



- **Energy density**
 - Electrolytes for 5V cathode materials
 - Electrolytes for 3V EDLCs

- **Cycle and calendar life**
 - Next generation SEI-film forming additives
 - Additives to scavenge detrimental impurities (HF, H₂O,...)



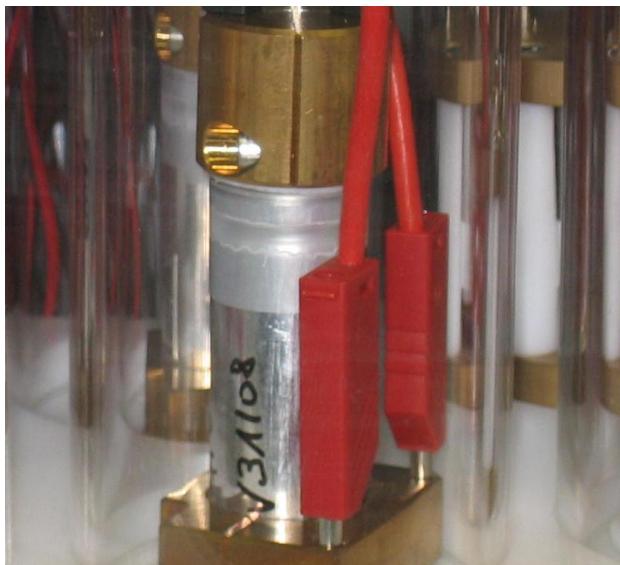
Li-Ion Battery Electrolytes

Electrochemical Characterization



Typical test procedures

- Basic characterization
 - Conductivity
 - Electrochemical stability using Cyclic Voltammetry
 - Thermal stability studies via DSC, DTA
- Battery test
 - Cycle Life
 - Rate capability

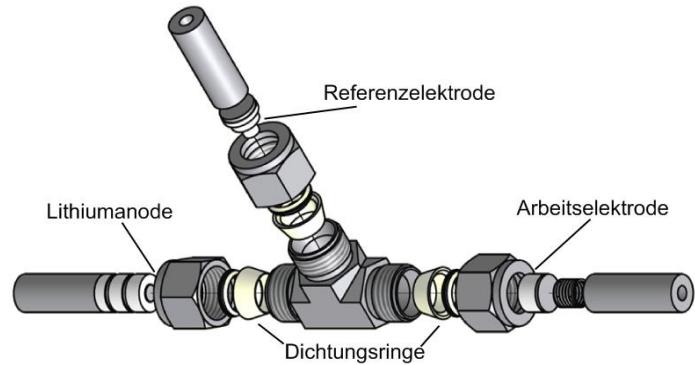


Li-Ion Battery Electrolytes

Half-Cell-Test vs. Full-Cell Tests

Half-Cell-Test

- **Advantages**
 - Simple setup
 - Fast material screening possible
- **Major Limitation**
 - Lithium metal electrode strongly influence results
 - No reliable additive characterization or cycling test possible
 - Cell geometry is far away from real battery system
(keyword ratio electrolyte: electrode)



Full-Cell-Test

- **Advantages**
 - Reliable electrolyte characterization in combination with customer's electrode and separator material
 - Long-term cycling test, life time tests possible
(proven: > 800 cycles, 80% remaining capacity)
 - Influence of additives on cell performance
- **Major Limitation**
 - Complex setup



Electrolytes Optimization

Complex, Customer Specific, Time Consuming



- General situation
 - Electrolyte development is customer specific
 - Each customer use a special, unique, combination of cathode, anode, separator, cell geometry,...
 - There is a huge variety of different electrolyte materials
 - Actually, 5 major solvent (EC, PC, DMC, DEC, DEC) + some specialties
 - A constantly increasing number of additives
 - Increasing complexity with respect to conducting salts. Visible trend toward salt mixtures e.g. LiPF₆/LiBOB, LiPF₆/LiFAP,...
 - Electrolyte development is time consuming
- Challenge
 - Fast and reliable electrolyte adaptation to the customer's system and customer's needs

Electrolytes Optimization

DoE as a powerful tool to manage complexity II



Example Conductivity

$$\kappa = a_0 + \sum a_i c_i + \sum a_{ij} c_i c_j + \sum a_j^2 c_j^2$$

Major impact of component i

Interaction between different components i and j

Interaction between two components i

- Work pretty good for fundamental physical chemical and electrochemical properties
 - Conductivity
 - Viscosity
 - Boiling point, flashpoint
 - Electrochemical stability (in particular for supercap electrolytes)
- Further battery under development
 - Rate capability
 - ...
- Disadvantage
 - Highly reproducible, standardized tests necessary
 - No physical chemical model

Lithium-Ion Battery Electrolyte

Analytic and Quality control



- Water: < 20ppm Karl-Fischer-Titration
- HF: < 50ppm Non-aqueous titration
- Anions: Cl, SO₄,.. < 5ppm Ion chromatography
- Cations: Na, K, Ca, Fe,... < 10ppm ICP-OES
- Color < 50 Hazen/APHA
- Identity
 - Solvent mixture +/- 1%
 - Additive +/- 0,25%
 - LiPF₆ +/- 0,5%
 - Density +/- 0,01 g/ml



Specifications are agreed on individually with the customer

Summary



- **Today's battery electrolytes are complex multi-component mixtures**
 - 2 to 4 solvents
 - Up to 5 additives
 - LiPF₆ (in combination with additional Li-salt)
- **Electrolyte optimization is a time consuming, customer specific process**
 - It is recommended to test electrolyte in the customer specific environment (anode, cathode, separator)
- **Quality is a critical issue**
 - Specifications have to be agreed on individually

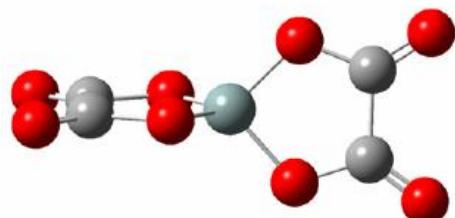




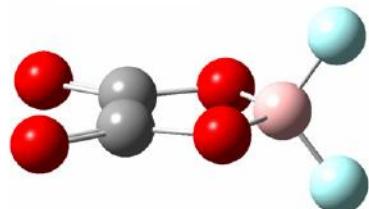
Backup

Conducting Salts

LiBOB, LiDFOB, and LiFAP



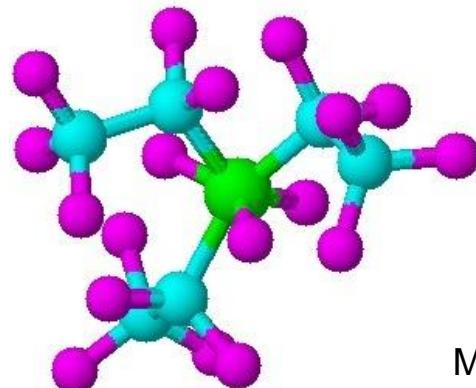
Chemetall



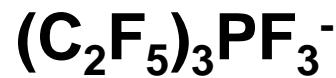
Central Glass



Lithium-Bis-Oxalato-Borate, LiBOB
Lithium-Difluoro-Oxalato-Borate



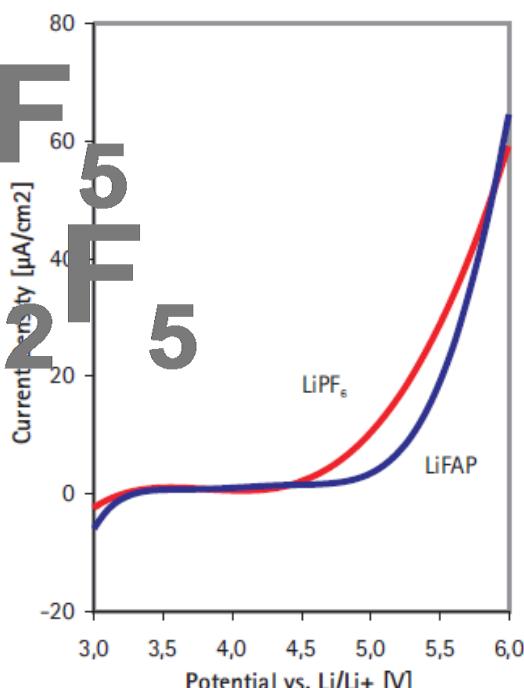
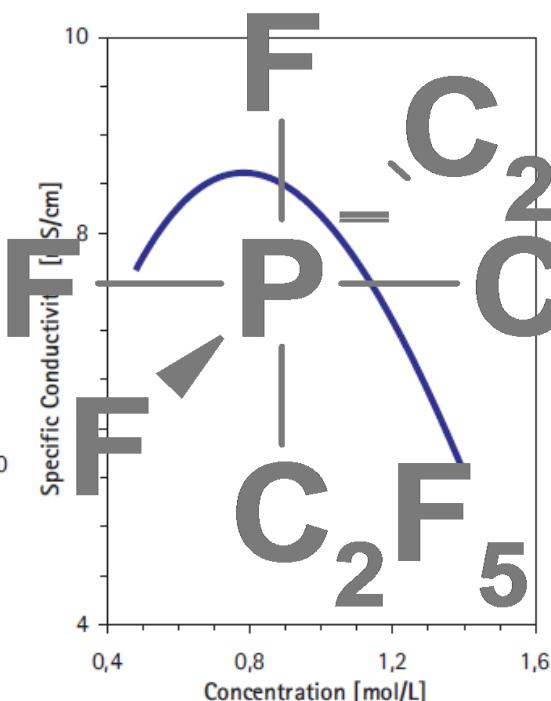
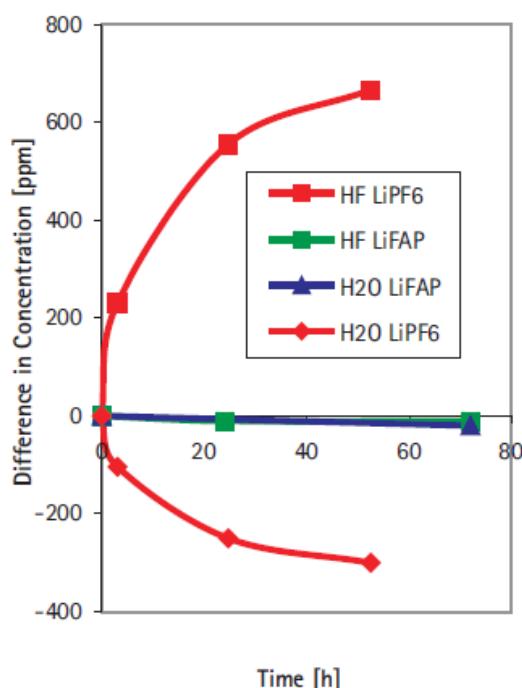
Merck



Lithium-Tris(pentafluorethyl)-
Trifluor-Phosphate
LiFAP

$\text{Li}(\text{C}_2\text{F}_5)_3\text{PF}_3$ LiFAP

Excellent (Electro)chemical Stability



- No sensitivity towards hydrolysis
- Conductivity comparable to LiPF₆ electrolytes
 - EC:DMC (1:1) @ 20°C: 8-9 mS/cm
- High electrochemical stability
 - At least comparable to LiPF₆

Additives

The difference between „just standard“ and „advanced“

Solvent/Additive	LUMO/eV	Reduction Potential (vs. Li ⁺ /Li)	
		on GC	on GR
	VC	0.10 -0.14	1.4
	ES	0.035 0.03	1.6 1.8~2.1
	SC	0.186	1.6
	N-chlorosuccinimide (CSC)	-0.527	3.2 > 2.5
	CC	1.10	
	2-acethoxy-4,4-dimethyl-4-butanolide	0.688	1.3~1.1

Anforderungsprofil HEV Batterie:

- Lebensdauer Batterie: > 10a
- 1. Ladung pro Tag
- Endkapazität: 80%

„Ausbeute“: > 99,99%/Zyklus