

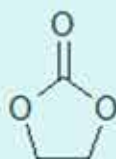
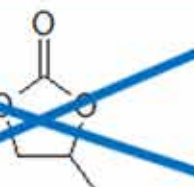
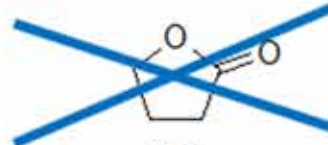

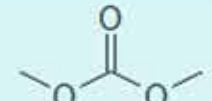
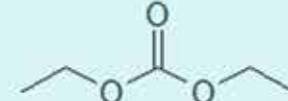
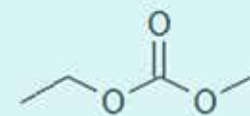
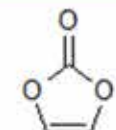
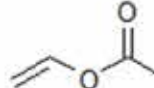
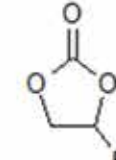
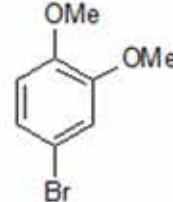
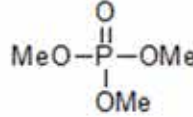
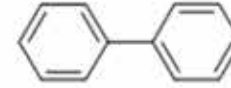
Lithium-Ion Batteries and Beyond

Prof. Martin Winter, MEET Battery Research Center,
Institute for Physical Chemistry, University of Münster, GER

Helmholtz Institute “Ionics in Energy Storage”
Forschungszentrum Jülich GmbH, GER

IV. Electrolytes

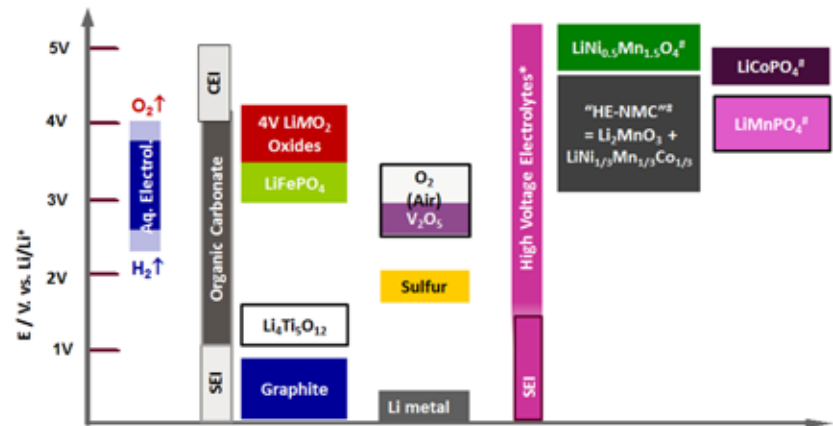
1. Composition of liquid organic-solvent-based electrolytes
2. Conductivity and transport mechanism
3. Electrolyte stability and interphase (SEI, CEI) formation
4. SEI and CEI analysis
5. SEI forming solvents and electrolyte additives
6. The electrolyte salt: LiPF_6
7. Ionic Liquids (ILs)

Salts	High Dielectric Solvents (HDS)	Low Viscosity Solvents (LVS)	Electrolyte Additives
<ul style="list-style-type: none"> ▪ LiPF_6 ▪ LiBF_4 ▪ LiCF_3SO_3 ▪ LiAsF_6 ▪ LiClO_4 ▪ $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ▪ $\text{Li}_2\text{B}_{10}\text{F}_{12}\text{H}_{12}$ <p>Toxic or Explosive or Corrosive or Not Well-Conductive</p>	<div style="border: 1px solid black; padding: 5px; margin-bottom: 10px;">  <p>EC</p> </div> <div style="text-align: center;">  <p>PC</p> </div> <div style="text-align: center;">  <p>GBL</p> </div> <p>Uneffective SEI</p>	<div style="text-align: center;">  <p>DME</p> </div> <div style="border: 1px solid black; padding: 5px; margin-top: 10px;">  <p>DMC</p>  <p>DEC</p>  <p>EMC</p> </div> <p>Oxid. Stability?</p>	 <p>VC</p>  <p>VA</p>  <p>FEC</p>  <p>DMBB</p>  <p>TMP</p>  <p>BP</p>

*M. Winter, Tutorial Book, Second International Symposium on LIBTA, Baltimore Inner Harbor, 2006

- The electrolyte composition has to be tailored to make high-voltage lithium batteries possible
- Aqueous electrolytes suffer from a low thermodynamic electrochemical stability window (ESW) of 1.23V, which can be extended by specific electrode and electrolyte measures to approx. 2V.
- Nevertheless, beyond 1.23V, electrolyte decomposition and gas evolution (H_2 and O_2) takes place.
- Non-aqueous organic-carbonate-solvent-based electrolytes provide a larger ESW, which can be kinetically extended by formation of SEI and CEI.
- Some low-voltage LIB chemistries, e.g., using $Li_4Ti_5O_{12}$ and $LiFePO_4$ with $\approx 2V$ cell voltage, may operate at voltages where the org. carbonate electrolyte is basically stable and no/little SEI and CEI formation takes place.
- '4V' LIBs rely on effective SEI and CEI.
- Li-metal battery chemistries, such as Li/sulfur and Li/air (O_2) need an SEI on the Li-metal side.

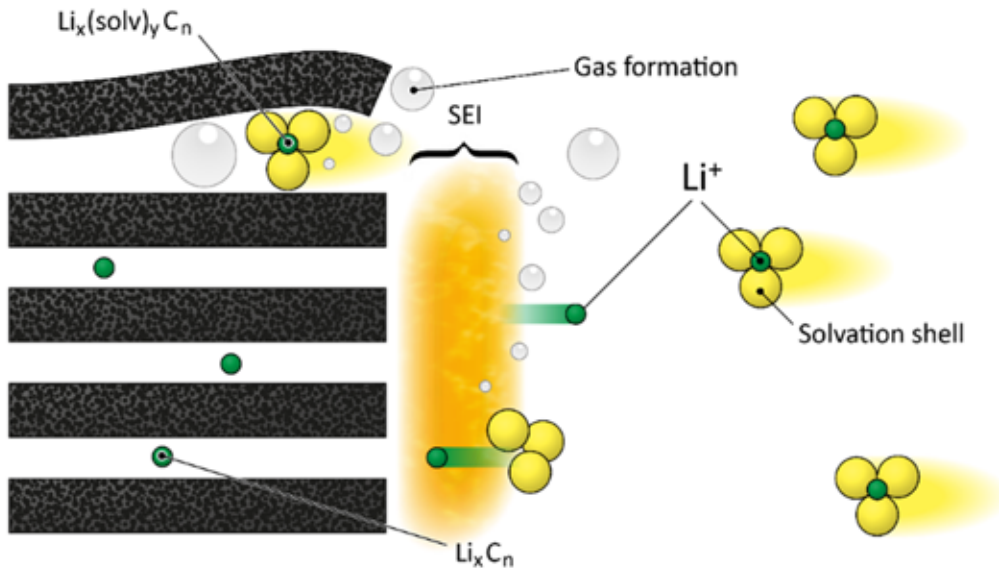
- Increasing the voltage by using high-voltage cathodes, e.g. $LiNi_{0.5}Mn_{1.5}O_4$, $LiCoPO_4$, etc. asks for new electrolytes, since the typical organic carbonate solvents are not stable enough and/or the CEI is not effective at the higher potentials.
- High-voltage electrolytes can be designed using fluorinated solvents, nitriles, etc.
- Nevertheless, an effective SEI is also necessary in the case of high-voltage electrolytes.



*e.g., fluorinated solvents & ionic liquids, nitriles, sulfones, etc.

(Magnified figure on the next slide)

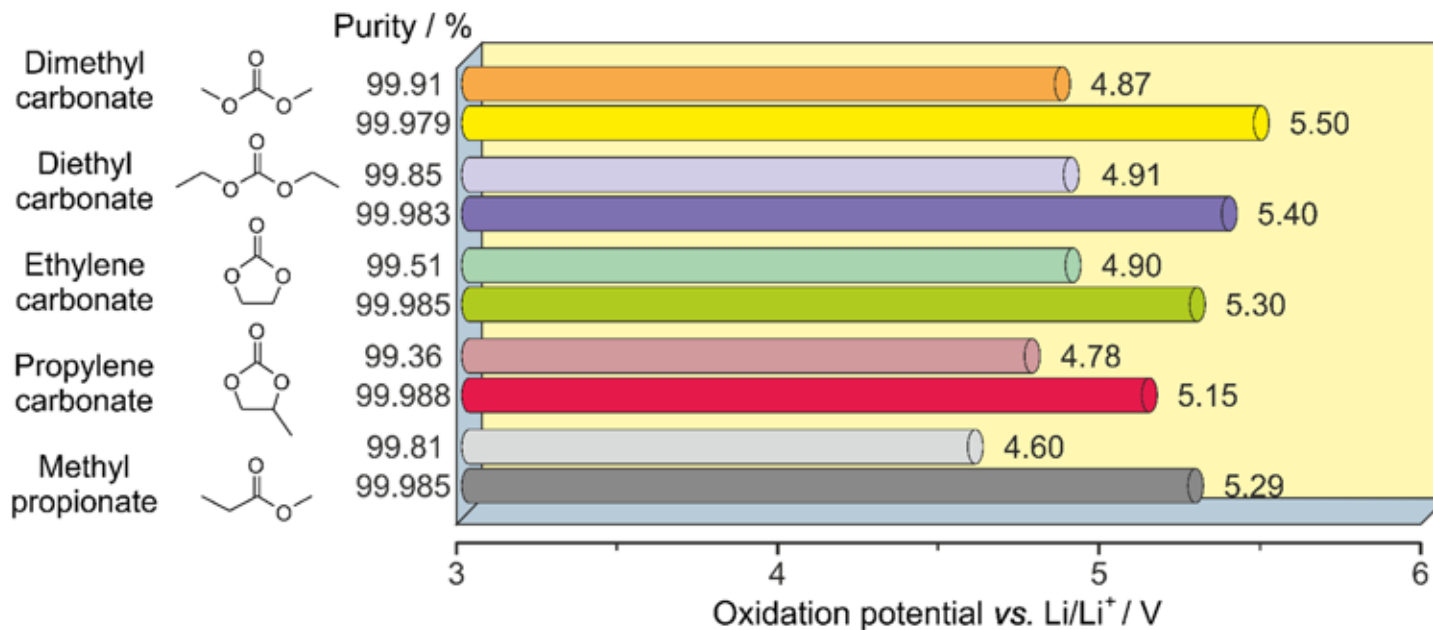
Electrolyte decomposition and SEI formation



- Presently, all liquid organic electrolytes, incl. the typically used organic-carbonate-solvent-based electrolytes, are thermodynamically not stable against reduction.
- Kinetic stability requires an effective SEI. For properties of the SEI, please refer to chapters 'Introduction' and 'Anode'.
- SEI formation in organic-carbonate-solvent-based electrolytes is accompanied by side reactions, such as
 - (i) solvent co-intercalation → $\text{Li}_x(\text{solv})_y$, and
 - (ii) gas formation.
- Typical gases that evolve during reduction: hydrogen (H_2), ethylene ($\text{H}_2\text{C}=\text{CH}_2$), methane (CH_4) and carbon monoxide (CO).

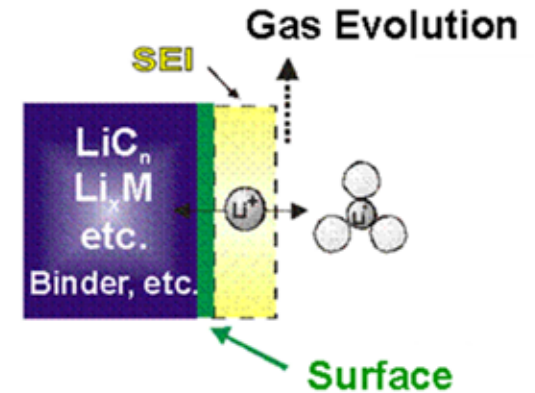
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- Organic-carbonate-(EC, EMC, DMC, DEC)-solvent-based electrolytes decompose at potentials beyond ≈ 4.3 V vs. Li/Li⁺.
- Decomposition generates gases (e.g., CO₂) and H⁺, reacting with LiPF₆ to HF!
- A few electrolyte solvents with high oxidation stability, e.g., nitriles, fluorinated solvents, ionic liquids
- Practical experiments reveal that oxidation potentials depend on solvent purity:



- Higher purity → Better oxidation stability, but purification increases costs.

Electrolyte (EL) consists basically of solvents and salt, e.g., **1M LiPF₆ in EC/DMC**



(Simple) Examples:

Decomposed Species	Origin	Effect on Performance
Gases: $\text{CH}_2=\text{CH}_2$, H_2 , CO	Solvent(s)	Increase of cell pressure, EL solvent loss (drying out)
Polymers, e.g., PEO	Solvent(s)	SEI contribution, cell resistance, EL solvent loss (drying out)
LiF	LiPF ₆	Change of EL conductivity, SEI contribution, cell resistance
Li ₂ CO ₃ , (CH ₂ OCO ₂ Li) ₂ , CH ₃ OLi	Solvent(s) Li ⁺ (from cathode)	SEI contribution, cell resistance, Li capacity loss ⇒ Change of material balance in cell

They introduce a specific (= desired) "functionality" or "role" in the electrolyte system. A small amount (a few percent) only is needed in order not to change the bulk electrolyte properties.

("functional electrolyte", "role-assigned electrolyte")

- Electrolyte additives for anode passivation (SEI)
- Electrolyte additives for cathode protection (cathode SEI)
- Electrolyte additives for overcharge protection
- Electrolyte additives for wetting
- Electrolyte additives for flame retardation
- Electrolyte additives for trapping of undesired detrimental components
 - Other functions desired? Over-discharge protection, anti-aging, ...?
 - Numerous, uncountable patents and publications!
 - Practical electrolyte may contain more than 1 additive
 - Many secret ingredients in liquid electrolytes

Status: High dielectric solvents HDS EC (PC)... + low viscosity solvents LVS (DEC, DMC, EMC, ...)

Pros:

- Sufficient (but not great) interphase formation
- Good room-temperature conductivity

Cons:

- Low- and high-temperature performance limited: conductivity, wetting, viscosity,...
- Stability at elevated ($>\approx 40$ °C) temperatures is limited
- Safety, in particular flammability, is a concern
- Reactivity with electrodes \rightarrow decomposition and gassing
- Liquid can leak \rightarrow safety and performance concern
- Transference number of Li^+ is only: $t_{\text{Li}^+} \sim 0.33$ and less
- Unlike aqueous electrolytes: no chemical over-charge protection in solvent

Measures:

- Keep liquid organic-solvent-based electrolyte, but substitute or add novel solvent components and electrolyte additives (see above)
- Use of room-temperature molten salts \rightarrow 'Ionic Liquids'
- Solidification of the electrolyte (\rightarrow **see chapter on Post-Lithium-Ion Batteries**)
 - Immobilize liquid electrolyte, e.g., in a polymer matrix (hybrid or 'gel' electrolyte)
 - Substitute liquid organic-solvent electrolyte, e.g., with a ceramic or polymer electrolyte

Electrochemical properties

- ✓ Wide electrochemical stability window, in particular good oxidation stability, but some SEI issues with anodes, such as graphite and Si
- ✓ Can dissolve numerous lithium salts, even in high concentrations
- High molecular weight → Lower specific energy than with organic-solvent-based electrolytes
- High viscosity, in particular with Li electrolyte salt → Lower ionic conductivity

Thermal properties



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Cost

- High cost of anions and of salt purification → Too high for mass use in LIBs
- ✓ Hydrophobic, less water sensitive
- ✓ Recycling is possible