

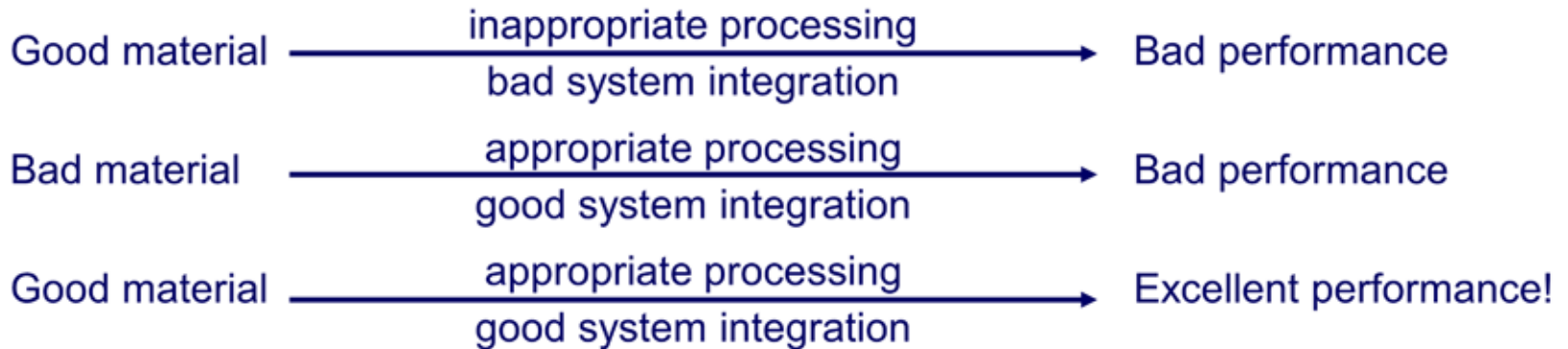
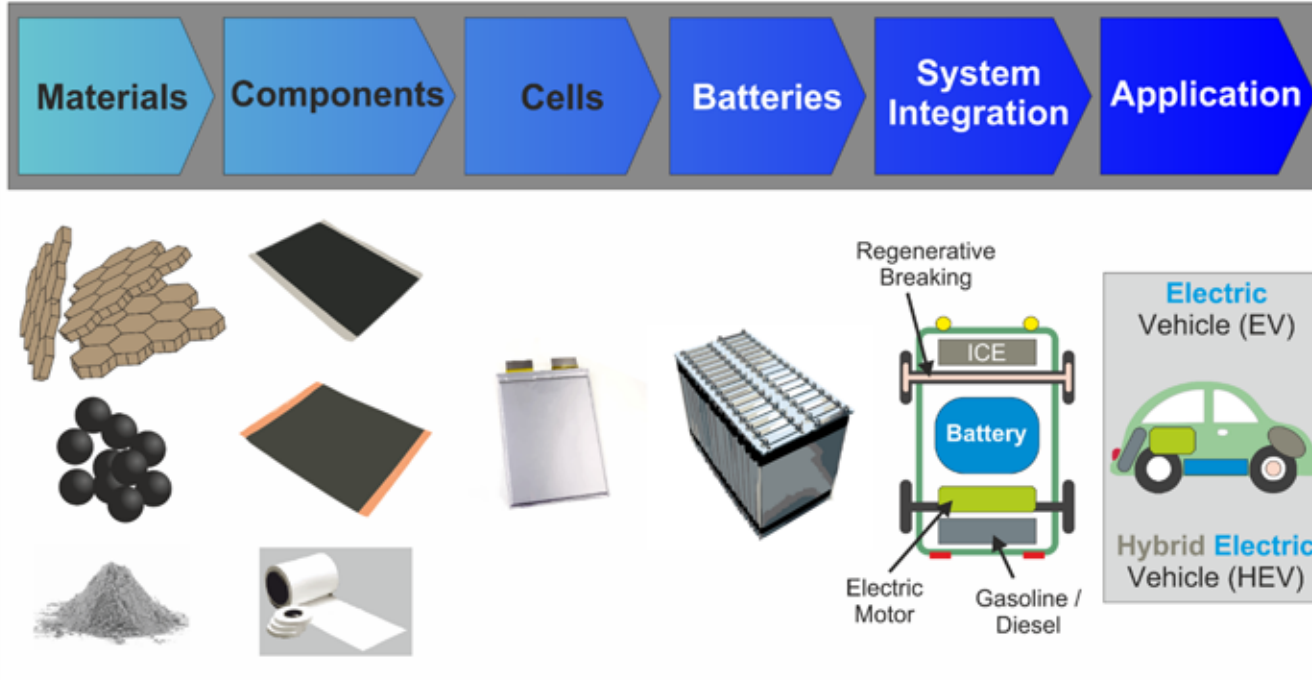
Lithium-Ion Batteries and Beyond

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I. Introduction

1. General principles
2. Li-metal chemistry—the ancestor of Lithium Ion
3. Lithium-Ion design overview
4. Battery design trade-offs and limitations



Active Anode and Cathode Materials:

Determine capacity and voltage \Rightarrow energy

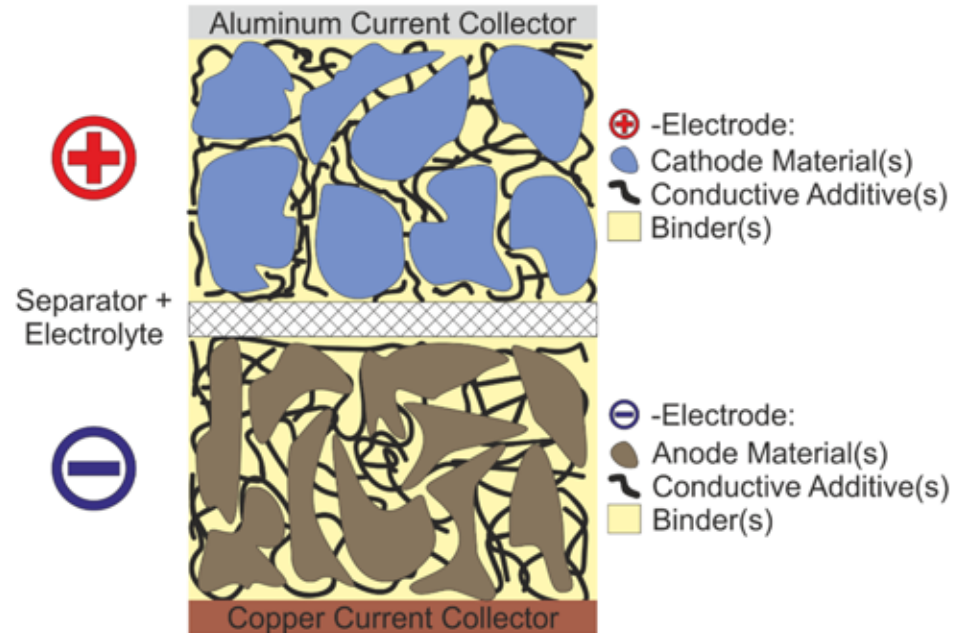
Inactive Materials:

Add, mass + volume \Rightarrow decrease energy

- ❖ **Electrolyte:** ion conduction, interfaces
- ❖ **Separator:** safety, electrode separation

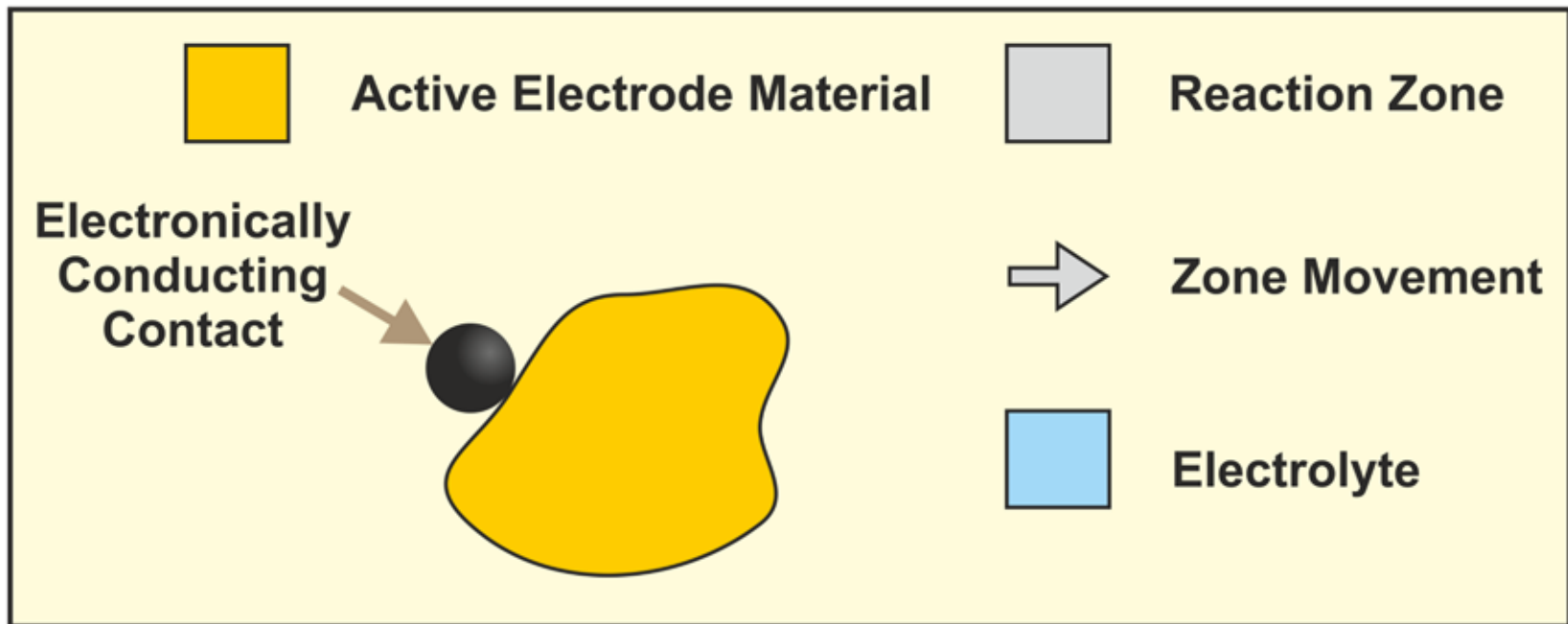
Electrode Inactive Components:

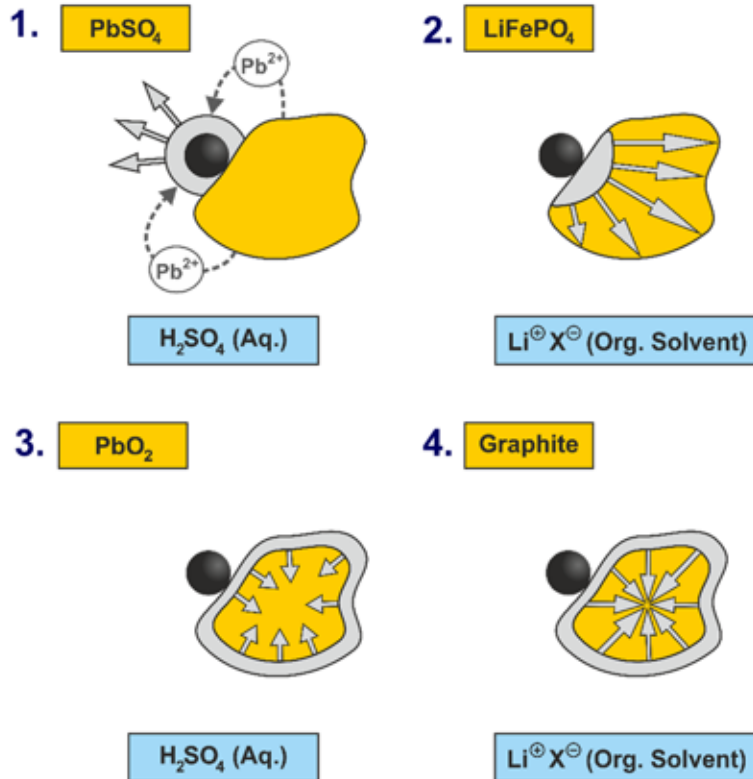
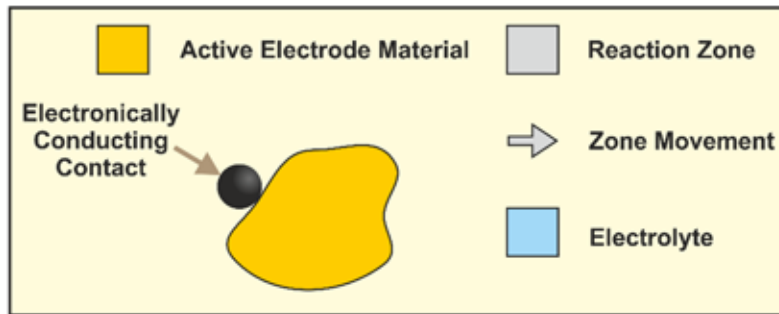
- ❖ **Current collector:** electron conduction, connection to the 'outside'
- ❖ **Conductive additive:** porosity, 'inside' electron current distribution
- ❖ **Binder:** The 'glue', that holds everything together
- ❖ **Processing solvents** (not treated here)



- The active material (AM) can be an electron conductor, ion conductor, electron and ion conductor, or does not show ion and electron conductivity at all.
- Different electron and ion transport properties of the AM → different reaction mechanisms and reaction zone movements → cases 1- 4 (following 4 slides).
- Depending on the reaction mechanism, the electrolyte and electronically conducting agents play an essential role for battery performance.

Legend (for the following 4 slides):





Case 1:

Electron Conduction: **No**
 Ion Conduction: **No**
PbSO₄ in aq. H₂SO₄

Case 2:

Electron Conduction: **No**
 Ion Conduction: **Yes**
LiFePO₄ in Li⁺X⁻ (org. solvent)

Case 3:

Electron Conduction: **Yes**
 Ion Conduction: **No**
PbO₂ in aq. H₂SO₄

Case 4:

Electron Conduction: **Yes**
 Ion Conduction: **Yes**
Graphite C₆ in Li⁺X⁻ (org. solvent)



Ion Size

Ionization Energy (IE) =

Invested energy to oxidize alkali metal to alkali ion (in the gaseous state)

⇒ In gaseous state: Li is NOT the metal with lowest potential

Ionization Energy

Free Energy of Solvation

Free energy of solvation =

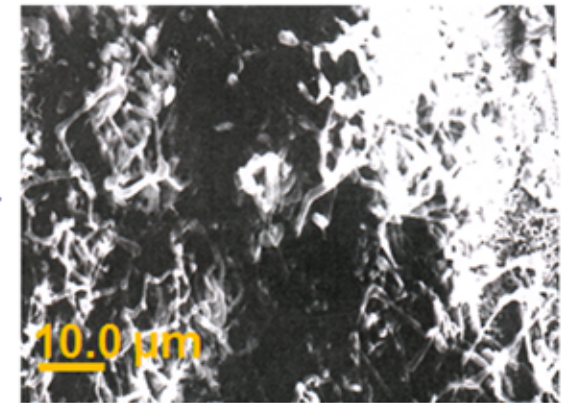
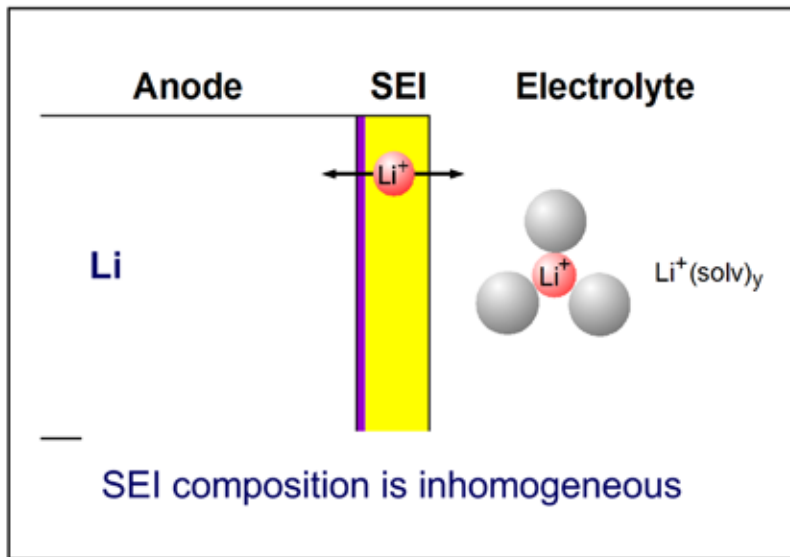
Released energy when ions associate with solvent molecules (solution state):

⇒ In solution: Li⁺ is strongly solvated

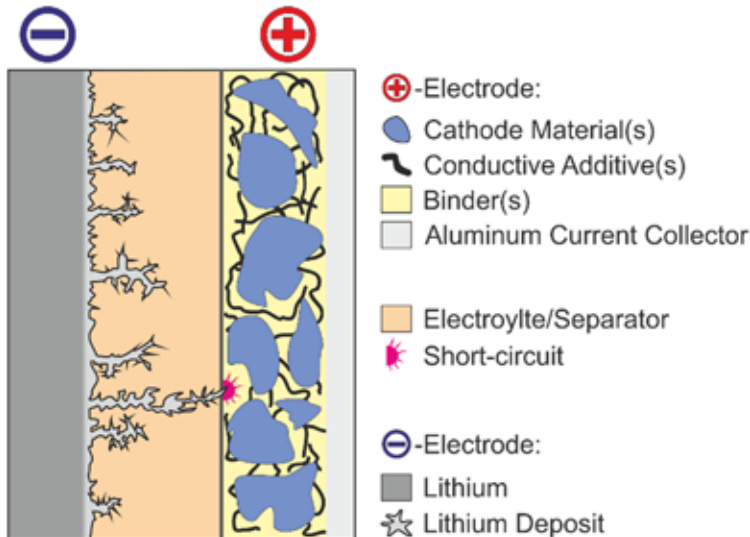
⇒ Important role of Li⁺ solvation and desolvation for rate capability

Electrode Potential

Li	Na	K	Rb	Cs	E / V vs. SHE
-3.04	-2.71	-2.93	-2.93	-2.92	



"Vicious Circle": Inhomogeneous SEI
 → Inhomogeneous Li deposition morphology
 → Inhomogeneous SEI → ...

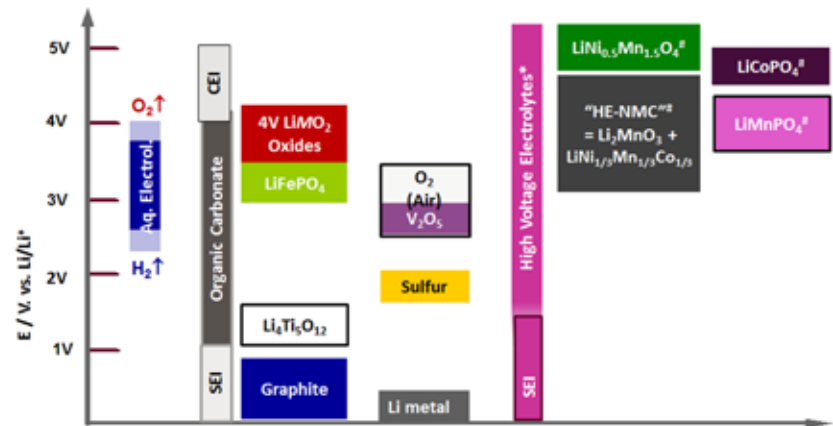


- Various Li deposition morphologies
- Needle-like morphology = Dendritic Li
- Dendrites grow to filaments → Short-Circuit → Thermal Runaway → ...
- Continuous surface changes, continuous electrolyte decomposition and SEI formation
 → Formation of high-surface-area Li (HSAL)
 → Safety and performance problem!
 ⇒ Li metal replacement necessary!

- 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) take place.

- 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, as 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, in the case of high-voltage electrolytes also, an effective SEI is necessary.

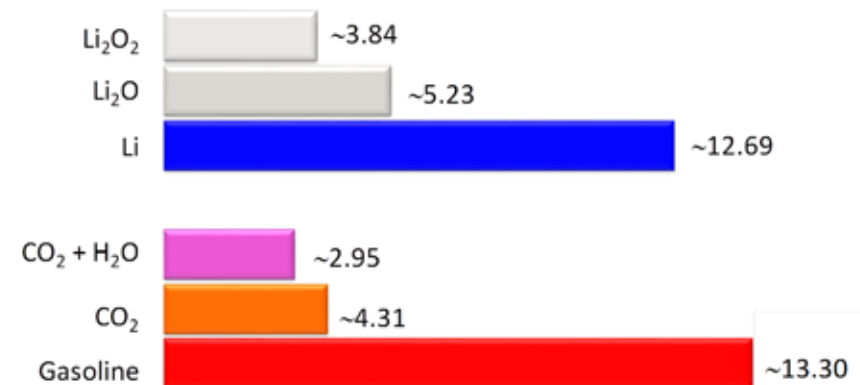
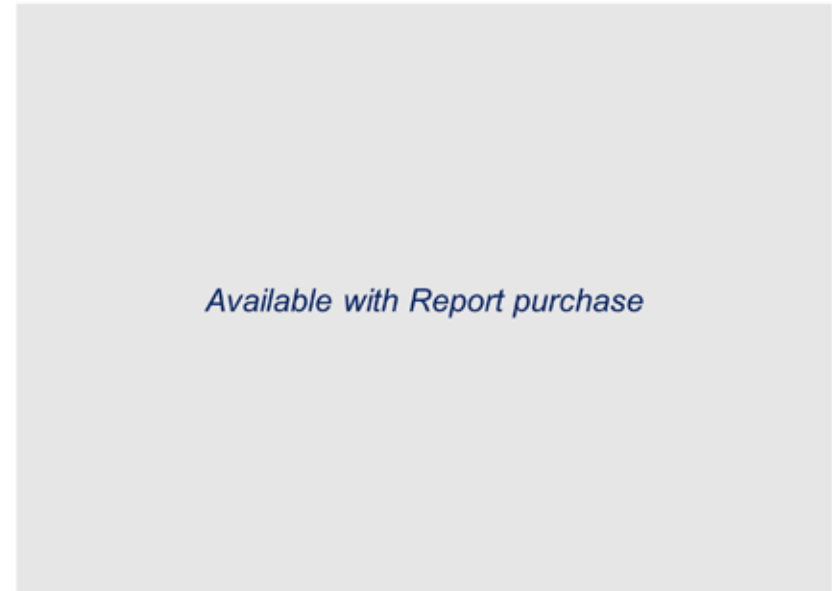
Available with Report purchase



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

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- Without considering the weight of the reaction products, Li and gasoline have similar energy densities (numbers in kWh/kg).
- The accumulation of solid Li_2O_2 or Li_2O during discharge of a Li/air battery increases the battery weight and thus decreases the energy density. Values for the fully discharged state are shown.
- If, hypothetically, the reaction products (CO_2 or $\text{CO}_2+\text{H}_2\text{O}$) of gasoline combustion were collected as well, the energy density would correspondingly decrease as indicated.
- Gasoline is lightweight compared to oxygen. The heavyweight combustion products CO_2 and water are continuously exhausted from the ICE.
- The reaction partner oxygen does not contribute to system weight.



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- Electrochemical energy storage and conversion devices operate beyond the thermodynamic stability of the electrolyte, i.e., undesired side reactions can occur at the electrode/electrolyte interfaces, e.g., surface reaction and passivation.
- Side reactions deteriorate electrode and thus cell performance.
- Nano-materials possess large surface areas.
- Impact of these side reactions increases with the surface area → **'bad nano'**
- Nano-particles show a larger surface area than nano-structured macro-particles.

