Rechargeable Batteries for Electrochemical Energy Storage: From Battery Research to Application

Workshop: Batteries – Fuelling the Alliance with the Future
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Münster Electrochemical Energy Technology

Diversity and Internationality
About 140 staff members from more than 12 nations, 30% female

Worldwide Visibility
with numerous scientific publications, conference contributions, patents, awards, etc.

Bridge
from Science to Industry

Official Launch
in 2009 – Entry into MEET-Arcades in 2011

Central Scientific Institution
of University of Münster since 2013
MEET Battery Research Center: Division „Materials“

Head of Division “Materials”: 
Dr. Tobias Placke

Deputy Head: 
Dr. Richard Schmuch

Group size (2018): 
- 5 Post Docs
- 15 PhD students
- > 15 Undergraduate Students (Master, Bachelor or internship students)

November 6, 2018

https://www.uni-muenster.de/MEET/team/index.html
Global market for lithium ion batteries (LIBs) in xEVs (HEVs, PHEVs, BEVs, etc.) and energy storage applications is huge.

xEV market based on LIB technology has recently become the largest.
The Lithium Ion Battery (LIB): A Success Story

Cellular Phones sold per Year (Million)

- Li-ion
- NiMH

Tons of cathode active materials

- 2000
- 2017

Li-ion 18650 cell price ($/Wh)

- 2000
- 2017

(1) Pillot, C. Talk at Advanced Battery Power, Münster 2018.
From Today’s View: Is it possible to develop a “1000 km battery”?

Yes, but…
Battery Performance Targets: Energy Density and more

Physicochemical limit: $\approx 400$ Wh/kg, $\approx 800$ Wh/L

- LIBs (intercalation/insertion) approach physicochemical limit:
  - Current energy density: $\approx 260$ Wh/kg & $\approx 700$ Wh/L in cylindrical 18650-type cells
  - Further energy-optimization becomes increasingly difficult

Roadmap of key performance parameters for automotive application (from OEM perspective)

- **Power [W]**
  - (10x, 50°C, 25°C)
- **Low T power [W]**
  - (10x, 50°C, -20°C)
- **Safety [EUCAR level]**
- **Cost [%]**
- **Charging current [A]**
- **Lifetime [cycles@ten years]**

*: pack level

Battery Performance Targets: Energy Density and more

Performance parameters are affecting each other and need to be well balanced!

Roadmap of key performance parameters for automotive application (from OEM perspective)\(^{(3)}\)

*: pack level

November 6, 2018

The Battery Value Chain: From Material Level to Pack Level

Material level (active materials) → Electrode level (binder, conductive additive, current collectors) → Cell level (separator, cell housing, etc.) → Module level (module container, control units, sensors, etc.) → System or Pack level (battery management system, cooling, etc.)

Addition of inactive materials: Decrease of energy content

Lithium ion battery (from OEM perspective)

Battery Process Chain

Copper 8 µm
Porous composite insertion electrode 65 µm
Liquid electrolyte Porous separator 20 µm
Porous composite insertion electrode 65 µm
Aluminum 12 µm

The Battery Value Chain: From Material Level to Pack Level

- Material Processing
- Component Production
- Cell Production
- Module Production
- Pack Assembly
- Vehicle Integration
- Recycling or 2nd Life

Increasing potential to improve key performance indicators

Lithium ion battery (from OEM perspective)

Specific energy / Wh/kg

- today
- 2025

Cost Structure of Lithium Ion Batteries: Raw Material Impact

Raw material cost account for ≈50-70% of LIB cells

Cathode materials are the most substantial contributor to material cost

Materials for Lithium Ion Batteries: State-Of-The-Art and Development Strategies

Cathode Materials (Lithium/Lithium-Ion)

- "3V"
- "4V"
- "5V"

Anode Materials (Lithium/Lithium-Ion)

- Li$_4$Ti$_2$O$_12$ (LTO)
- Metal Oxides (Conversion Materials)

Graphite
- Carbons
- Sn-C Composites
- Tin (Sn)
- Si-C composites

Spec. Capacity / Ah kg$^{-1}$

Potential vs. Li/Li$^+$ / V

- Li$_2$MnO$_3$/(1-x)LiMO$_2$ (M= Mn, Ni, Co)
- LiNi$_{0.5}$Mn$_{1.5}$O$_3$ (LNMO)
- LiCoPO$_4$ (LCP)
- LiMnPO$_4$
- Li$_2$FeSiO$_4$, Organic Cathodes
- LiCoO$_2$, Li[Ni$_x$Co$_y$Mn$_{2-x}$]O$_2$ (NMC), Li[Li$_{0.2}$Co$_{0.15}$Al$_{0.05}$]O$_2$ (NCA)
- LiMn$_2$O$_4$ (LMO)
- LiFePO$_4$ (LFP)

Materials for Lithium Ion Batteries: State-Of-The-Art and Development Strategies

Cathode Materials (Lithium/Lithium-Ion)

- "5V": $x \text{Li}_2\text{MnO}_3/(1-x)\text{LiMO}_2 (M= \text{Mn, Ni, Co})$
- "4V": $\text{LiCoO}_2$, $\text{Li}[\text{Ni}_{x}\text{Co}_y\text{Mn}_z]\text{O}_2$ (NMC), $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}]\text{O}_2$ (NCA)
- "3V": $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$ (LNMO)

Anode Materials (Lithium/Lithium-Ion)

- Graphite
- Si-C composites
- Silicon (Si)

Spec. Capacity / Ah kg\(^{-1}\)

Potential vs. Li/Li\(^+\)/V

State-of-the-Art LIB Anode Materials: Graphitic Carbons

- Carbonaceous materials: Synthetic graphite (SG; share of 54%) and natural graphite (NG; share of 39%) as well as amorphous carbons (share of 2%)

- Often, mixtures of amorphous and graphitic carbons are used to optimize the P/E-ratio

- Demand for graphite increases fast, especially for synthetic graphite due to EV market

- SG shows outstandingly high levels of purity and less fluctuating quality compared to NG → SG meets EV lifetime requirements

- Cost: ≈7 $/kg for NG and ≈13 $/kg for SG (2017)

- Currently, only some commercial cells (e.g. Panasonic) use silicon (SiO_x) in small amounts (few wt.%)

(1) Data from: Pillot, C. Talk at Advanced Automotive Battery Conference (AABC) Europe, Mainz 2018.
Industrial Production of Carbons: Synthetic Graphite vs. Natural Graphite

Major Challenges:

- High energy consumption and high cost, i.e. >25% of total production cost (synthetic graphite)
- Natural graphite is classified as „critical“ material (largest deposits: China)
- Purification of natural graphite is often done by acid treatment (HF) → water pollution
- China: insufficient monitoring and measures: high levels of environmental and air pollution

1) Mining and Flotation
- Mining from graphite ore
- Mechanical separation
- Flotation, drying, screening

2) Material processing
- Micronisation
- Spheroidization
- Purification (chem./therm.)

3) Particle Refinement
- Conditioning, grinding
- Classifying

**Petroleum coke, coal tar pitch**

1) Pre-treatment
- Calcination: „Soft Carbon“
- Crushing, grinding
- Classifying

2) Graphitization
- T ≥ 2800 °C

**Graphite ore**

1) Mining and Flotation
- Mining from graphite ore
- Mechanical separation
- Flotation, drying, screening

2) Material processing
- Micronisation
- Spheroidization
- Purification (chem./therm.)

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- Classifying, carbon coating

**Natural graphite**

Synthetic graphite

- Pre-treatment
  - Calcination: „Soft Carbon“
  - Crushing, grinding
  - Classifying

- Graphitization
  - T ≥ 2800 °C

- Material processing
  - Micronisation
  - Spheroidization
  - Purification (chem./therm.)

- Particle Refinement
  - Conditioning, grinding
  - Classifying, carbon coating

(2) The Washington Post: In your phone, in their air. [https://www.washingtonpost.com]
Industrial Production of Carbons: Synthetic Graphite vs. Natural Graphite

Strategies:

- Decrease of processing cost by decrease of energy consumption during graphitization: Catalytic graphitization

- Search for alternative, abundant precursor materials for synthetic graphite production (e.g., from biomass or waste products)

- Search for environmentally friendly (or friendlier) processes for natural graphite purification

- Recycling of graphite anode materials from spent lithium ion cells

Graphite Recycling from Spent Lithium Ion Cells

Charge/discharge cycling until 70% SOH

thermal purification

Reuse as graphite anode

Panasonic CGR18650CH Li-ion MH12210 cell


Graphite Recycling from Spent Lithium Ion Cells

Charge/discharge cycling until 70% SOH

Open questions / challenges:
- Impact of electrolyte/salt residues on long-term performance (stability and rate)?
- Impact on solid electrolyte interphase (SEI) formation and stability?
- Multiple recycling of graphite possible? Degradation effects?

Challenges and Strategies for Si-Based Anodes

- High volume changes during lithiation/de-lithiation
- Pulverization/”cracking” of Si particles
- Contact loss of particles from electronically conductive network or current collector
- Instability of solid electrolyte interphase (SEI): Breakage and re-formation
- High active lithium losses by continuous electrolyte decomposition (low Coulombic efficiency)

Strategies

- Active/inactive matrix concept (nano-Si in inactive matrix)
  - Si/Carbon composite materials
  - Si/intermetallics/carbon composite materials

3M approach:

State-of-the-Art LIB Cathode Materials

- LCO is mostly used for handheld consumer electronics (pouch cell lithium ion cells for mobile phones, tablets, etc.)
- NCM is used in other electronic devices and in large cells (EV applications)
- NCA is primarily used in 18650 cells (Panasonic, Tesla) and as blend with LMO for EV cells
- LMO is typically blended with NCM for EVs to adjust the P/E ratio:
  Trend: LMO/NCM 75:25 → LMO/NCM 25:75
- LFP is primarily used for EVs and electric buses in China, as well as for industrial or stationary applications

Cathode materials (2016): >270 000 tons
- LCO 14%
- NCM 31%
- NCA 9%
- LMO 8%
- LFP 38%

Cathode materials perspective (2025): 850 000 tons
- LCO 6%
- NCM 68%
- NCA 10%
- LMO 1%
- LFP 15%

State-of-the-Art LIB Cathode Materials: NCM-based Layered Oxides

NCM111 (Gen2a)  NCM523 (Gen2b)  NCM622 (Gen2b-3a)  NCM811 (Gen3a)  NCM910 (Gen3a/b)

Increasing nickel content

Increasing capacity

Ni: 33%  Ni: 50%  Ni: 60%  Ni: 80%  Ni: 90%
Co: 33%  Co: 20%  Co: 20%  Co: 10%  Co: 10%
Mn: 33%  Mn: 30%  Mn: 20%  Mn: 10%  Mn: 0%

- NCM523 and NCM622 (and NCA) can be considered as state-of-the-art materials for xEV applications
- NCM811: short-term goal for EV applications
- Higher Ni-content
  - Lower cost of raw materials
  - Challenges: Safety, lifetime and manufacturing

State-of-the-Art LIB Cathode Materials: NCM-based Layered Oxides

- **Cost drivers:**
  - Lithium is not considered as potential cost driver\(^{(2)}\)
  - Cost increase risk: especially Cobalt and Nickel pricing

- **Increasing nickel content**
  - NCM111 (Gen2a)
  - NCM523 (Gen2b)
  - NCM622 (Gen2b-3a)
  - NCM811 (Gen3a)
  - NCM910 (Gen3a/b)

- **Increasing capacity**
  - Ni: 33% Ni: 50% Ni: 60% Ni: 80% Ni: 90%
  - Co: 33% Co: 20% Co: 20% Co: 10% Co: 10%
  - Mn: 33% Mn: 30% Mn: 20% Mn: 10% Mn: 0%

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- NCM811: short-term goal for EV applications
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\(^{(1)}\) Noh, H.-J.; Youn, S.; Yoon, C. S.; Sun, Y.-K. Journal of Power Sources 2013, 233, 121.
Volumetric energy density [Wh/L] is of higher importance for mobile applications than specific energy [Wh/kg].

With respect to cathodes:
- High capacity
- High redox potential
- High material density

LNMO: High-voltage spinel (HVS; LiNi_{0.5}Mn_{1.5}O_4)
LRNMC: Li-rich NMC (HE-NMC; x LiMO_2 \cdot (1-x) Li_2MnO_3)

Motivation: Energy density [Wh/L]
Promises of High-Capacity/High-Voltage Cathode Materials

Motivation: Energy density [Wh/L]

Potential vs. Li/Li+ [V]

Volumetric Capacity [mAh/cm³]

Specific Energy [Wh/kg]

Energy Density [Wh/L]

Energy Efficiency [%]

LMO: 4.0 V
LNMO: 4.7 V
NMC-111: 3.7 V
NMC-811: 3.7 V
NCA: 3.7 V
HE-NMC: 3.4 V

LNMO: High-voltage spinel (HVS; LiNi₀.₅Mn₁.₅O₄)
LRNMC: Li-rich NMC (HE-NMC; x LiMO₂ · 1·x Li₂MnO₃)

State-of-the-art Electrolyte: Mixtures of Carbonates and LiPF$_6$

**Electrolyte Solvents**

**Step 1: Precursor via C1 and C2 Route**
- C1: Synthesis gas (CO + H$_2$) → Methanol → O$_2$ → Ethylene oxide
- C2: Ethylene → Ethylene oxide

**Step 2: Solvent Preparation**
- DMC → DEC
- CO → CO$_2$
- EtOH → EC

**Step 3: Electrolyte Preparation**
- Typical electrolyte contains:
  - 12.6% by weight Salt
  - 0-10% by weight Additives
  - ~85% by weight Solvent

**Electrolyte Salt (LiPF$_6$)**

**Step 1: Mining and Precursors**
- LiF(s)
- Li$_2$CO$_3$(s)

**Step 2: Salt Manufacturing Process**
- AHF (l) → LiF(s) → LiPF$_6$(s) purified

Current research focuses on novel additives for interface stabilization:
- **Anode**: Solid electrolyte interphase (“SEI”)
- **Cathode**: Cathode electrolyte interphase (“CEI”)
- **High voltage (>4.5 V)** electrolyte additives and solvents

Technological Roadmap of Battery Cell Chemistries

**Generation 5**
- Cathode: LFP, NCA
- Anode: 100% Carbon

**Generation 4**
- Cathode: NCM111
- Anode: 100% Carbon

**Generation 3a**
- Cathode: NCM523 to NMC811
- Anode: Carbon + Si (5-10%)

**Generation 3b**
- Cathode: HE-NCM, HVS
- Anode: Silicon/carbon

**Generation 2b**
- Cathode: NMC622 to NMC622
- Anode: 100% Carbon

**Generation 2a**
- Cathode: NCM111
- Anode: 100% Carbon

**Generation 1**
- Cathode: LFP, NCA
- Anode: 100% Carbon

Advanced lithium ion cells

2) Risk of earlier market entrance

First application date in EV

(1) Adapted from: Nationale Plattform Elektromobilität (NPE), *Roadmap integrierte Zell- und Batterieproduktion Deutschland*, 2016.
Research & Development of Battery Technologies: Past, Present and Future

1991:

- The demand as well as the economic and social importance of rechargeable batteries increases rapidly (electronics, electro mobility, home storage, etc.)
- Versatile requirements: Significant diversification of battery technologies in the past >25 years

• The demand as well as the economic and social importance of rechargeable batteries increases rapidly (electronics, electro mobility, home storage, etc.)

• Versatile requirements: Significant diversification of battery technologies in the past >25 years

• Lithium ion batteries (LIBs): Global market in xEVs (HEVs, PHEVs, BEVs, etc.) and energy storage applications is huge and will be the largest in the near future

• LIBs approach their physicochemical limit in terms of energy: Next generation? Alternatives? New Cell Chemistries?
Performance Targets: Energy Density

- Different battery technologies will be available at the market in parallel
- Application-specific usage of different battery systems (e.g. high energy vs. high power)
- Evolutionary development of each specific battery technology
- Classification of battery technologies:
  - Lithium ion systems
  - Lithium metal systems (ASSB, Li/S, Li/O₂)
  - Other/alternative battery systems (Na, Mg, Ca, Al, Dual-ion, etc.)
Lithium Metal Anodes: Enabled by Solid Electrolytes?

Today's LIB

Insertion electrode reaction principle

Shape change electrode reaction principle

Li-Metal based All-solid-state Battery

Copper

Porous composite insertion electrode

Liquid electrolyte Porous separator

Porous composite insertion electrode

Aluminum

8 µm

65 µm

20 µm

65 µm

12 µm

8 µm

20 µm

20 µm

65 µm

12 µm

Aluminum

Composite insertion electrode

Solid Electrolytes: A Reality Check

**Expectations**

- Higher safety
- No cross-contamination of transition metals in electrode compartments (cross-talk)
- No dendrite formation, use of Li metal
- Higher voltages (higher energy density)
- Wide range of operation temperatures
- Long-term stability (cycle life, calendar life)
- Less expensive materials for inactive materials (current collection)
- Simplified thermal management

**Unsolved Problems**

- Slow kinetics in electrodes
- Ionic conductivity in electrodes
- Volume changes in electrodes
- „Dendrite“ formation
- Interfacial resistances
- Interfacial delaminations
- Enhanced deterioration during cycling
- Higher cost
- Battery design
Estimated Electrode Stack Energy Density

Amount of excess Li should be minimized for:
- high energy density [Wh/L]
- minimal costs [$/kWh]

Conclusion

- Roadmaps have identified the **dominant technology** for the next decade(s): The **lithium ion technology** (with or without solid electrolyte).

- There will be **no universal LIB technology** for all application purposes, but rather a variety of chemistries and configurations for specialized applications.

- The highest potential to improve key performance indicators (energy, cost, etc.) of LIBs is on the **material level**.

- Most promising strategies for **energy density improvements of LIBs** are the implementation of higher Si-contents in high-energy anodes as well as to increase the Ni-content of layered cathode materials.

- Li-metal based chemistries, in particular **all-solid-state-batteries** can further enhance the **energy content**. However, it will be **challenging to be cost competitive** to further improved LIBs.

- Novel **sustainable technologies “beyond lithium”** have been explored, such as batteries based on monovalent (Na⁺, K⁺) and multivalent (Mg²⁺, Ca²⁺, Al³⁺) ions. However, it will be challenging to compete with advanced LIBs in terms of energy content and/or cost per energy.

- Foreseen 10% yearly increase in the number of batteries produced will inevitably need recycling to recover metals/materials whose abundance is limited: **efficient recycling of materials** is mandatory.
“Nothing great was ever achieved without enthusiasm.”
Ralph Waldo Emerson, American Philosopher

Thank you for your attention!
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