Lithium-Ion Battery Materials
An Energy Storage Opportunity for Southern Africa

presented by Michael Thackeray

SA Energy Storage 2017
Emperors Palace, Johannesburg, South Africa

29 November 2017
Content

- A historical perspective
- Li-ion battery materials
- A Southern African opportunity
Dominant Battery Technologies since Volta (~1800)
(Theoretical values: masses of active electrode and electrolyte components only)

<table>
<thead>
<tr>
<th>Year</th>
<th>System</th>
<th>Negative Electrode</th>
<th>Positive Electrode</th>
<th>OCV (V)</th>
<th>Th. Cap (Ah/kg)</th>
<th>Th En. (Wh/kg)</th>
<th>Pr. En. (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1859</td>
<td>Plante</td>
<td>Lead-acid Pb</td>
<td>PbO₂</td>
<td>2.1</td>
<td>83</td>
<td>171</td>
<td>20-40</td>
</tr>
<tr>
<td>1866</td>
<td>LeClanché</td>
<td>Zn-MnO₂</td>
<td>Zn γ-MnO₂</td>
<td>1.6</td>
<td>*208</td>
<td>*333</td>
<td>85</td>
</tr>
<tr>
<td>1898</td>
<td>Jungner</td>
<td>Ni-Cd</td>
<td>Cd NiOOH</td>
<td>1.35</td>
<td>162</td>
<td>219</td>
<td>20-40</td>
</tr>
</tbody>
</table>

* Based on alkaline cell reaction: Zn + 2MnO₂ + H₂O → ZnO + 2MnOOH

1973-1974 MID-EAST OIL CRISIS
(Discovery of β-Al₂O₃ spawns high temperature Na/S and Na/MCl₂ (‘Zebra’) systems)

<table>
<thead>
<tr>
<th>Year</th>
<th>System</th>
<th>Electrode</th>
<th>OCV (V)</th>
<th>Th. Cap (Ah/kg)</th>
<th>Th En. (Wh/kg)</th>
<th>Pr. En. (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1989</td>
<td>Ni-MH</td>
<td>MH alloy</td>
<td>NiOOH</td>
<td>1.35</td>
<td>~178</td>
<td>240</td>
</tr>
<tr>
<td>1991</td>
<td>Li-Ion</td>
<td>LiₓC₆</td>
<td>Li₁₋ₓMO₂ (M=Co, Ni, Mn)</td>
<td>4.2-3.0 (3.8)</td>
<td>158 (for x=1.0)</td>
<td>584</td>
</tr>
</tbody>
</table>

BEYOND LITHIUM-ION
Li/S; Li/O₂, Na and Mg-based systems etc

- Li-ion cell chemistry extremely versatile – open to further advances
Thomas Edison (1847-1931)

- Prolific American inventor and enthusiast of electric power (>1000 patents)
- Ni-Fe battery (1901)

1896: Thomas Edison to Henry Ford: ‘Forget Electric Cars’

“Young man, that’s the thing; you have it. Electric cars must keep near to power stations. The storage battery is too heavy. Steam cars won’t do, either, for they require a boiler and fire. Your car is self-contained—it carries its own power plant’.

By the 1920s, EVs were out of vogue and had been replaced by ICEs

Battery Research at CSIR, South Africa (1974-1994)

- Prompted by the 1973-74 Oil Crisis
- Price of oil quadruples from $3 to $12 per barrel
- Government-funded research: 1974→
  - Lithium batteries – Li-ion spinel technology
- Contract research (De Beers, Anglo American): 1978→
  - High temperature Na/β-Al$_2$O$_3$/NaAlCl$_4$, FeCl$_2$ ‘Zebra’ batteries
- Technologically successful ideas – despite no battery experience in 1974
Chain of Events: 1983 - 2017

1983: Anglo American moves CSIR research team to a start up company in SA.

1985: Teams up with Daimler Benz to develop and implement Zebra batteries in electric vehicles.

1992: Zebra technology demonstrated in A-Class Mercedes and used in buses to transport athletes at the Barcelona Olympic Games.

1999: Anglo American and Daimler Benz walk away from a multi-million dollar investment in Zebra technology because of the lack of an EV market/infrastructure.
   - High temperature batteries for transportation also deemphasized by the US Department of Energy.

2017: Technology still alive – batteries for stationary storage being produced by FIAMM (Europe), GE (USA) in a joint venture with Chaowei Lvna (China).
Crude Oil Prices since 1861

1973: $3/barrel
1980: $36/barrel
1998: $12/barrel
1974: $12/barrel
2012: $112/barrel
2017: ~$50/barrel

Nominal
Real (2014 dollar) (inflation adjusted)

Wikimedia Commons: Data from *BP workbook of historical data*
Justification for EVs and Renewable Energy

CO₂ emissions – global warming

A planet in peril?

Population growth – a smaller world

Unsustainable tensions as mankind strives for equality and a share of resources

Impact of Li-Ion Batteries

- ~$23 billion market created over the past 25 years
  - Consumer electronics and communications
  - **Transportation** (‘Li economy’ driver)
    - Hybrid-electric vehicles and ‘plug-in’ HEVs
    - All electric vehicles
  - **Stationary energy storage** (grid, off-grid)
  - Implantable medical devices (Neuro-stimulators, pacemakers, defibrillators)
  - Aerospace, defense
  - Power tools, toys etc

- Lithium batteries have become a strategic commodity in national energy security
Global Li-ion Battery Market Predicted to be Worth ~$93 Billion by 2025

- Driven by e-mobility policies
- Volvo (Geely Holding) announces that from 2019 every Volvo vehicle would have an electric motor, EV, plug-in HEV or mild HEV (48V)
- Germany, France and UK call for a ban on traditional fuel vehicles by 2030-2040
Electrode materials market expected to increase fourfold within 10 years
The Advent of Li-Ion Batteries

*(Sony Corporation - 1991)*

- Lithium insertion/extraction reactions
- Highly energetic (4 V) systems
- Flammable electrolytes
- Inherently unsafe; individual cells are protected from overcharge by costly electronic circuitry
- Electrode and electrolyte materials dictate performance and safety

⇒ Scientific and technological motivation to find alternative materials
Li-Ion Batteries: 3.5 - 4 V Cathode Materials

ROCKSALT
LiMO₂
(M=Co, Ni, Mn)
LCO, NCA, NMC

- **Capacity limited** to ~0.5 Li per M atom (i.e., ~140 mAh/g)
- 2-D layers for Li⁺ transport
- Co⁴⁺ and Ni⁴⁺ unstable/highly oxidizing
- Structures destabilized at low Li content

SPINEL
LiM₂O₄
(M=Mn)
LMO

- **Capacity limited** to <0.5 Li/Mn at 4 V (i.e., <120 mAh/g)
- 3-D channels for Li⁺ transport
- Robust M₂O₄ spinel framework;
  - **High power electrode**

OLIVINE
LiMPO₄
(M=Fe)
LFO

- **Capacity limited** to 1 Li/Fe; P inactive (i.e., ~150 mAh/g)
- 1-D channels for Li⁺ transport
- Excellent structural and thermal stability
- Poor electronic and Li-ion conductivity
- Stable in nanoparticulate form
Li-Ion Batteries: Anode Materials

- **Carbon**
  - **Graphite**: <100 mV vs. Li\(^0\)
  - Moderate capacity (372 mAh/g)
  - Highly reactive, surface protection necessary

- **Metal Oxides**
  - **Li\(_4\)Ti\(_5\)O\(_{12}\)** (LTO) Spinel: 1.5 V vs. Li\(^0\)
  - Low capacity (175 mAh/g) and energy
  - High power
  - Safe!

- **Metals, Semi-metals and Intermetallic Compounds**
  - Al, Si, CoSn, Cu\(_6\)Sn\(_5\): <0.5 V vs. Li\(^0\)
  - High gravimetric/volumetric capacities
  - Large volume expansion on reaction with lithium
  - Reactive, surface protection required
  - Extremely challenging
Prognosis for Li-ion Technology

- Li-ion cells with:
  - Si or metallic Li anodes
  - effectively protected electrode surfaces
  - non-flammable electrolytes

would constitute significant advances in Li-ion technology that will take time to implement.

- In the interim, incremental advances in cathode design and performance can be expected.
Major Materials Challenges for Li-ion Batteries

- Increase the energy density of cells – both volumetric and gravimetric for portable/mobile applications
  - Increase cell voltage ⇒ e.g., LiMn$_2$O$_4$ (4 V) → LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (4.7 V)
  - Increase electrode capacity ⇒ Mn rather than Co-, Ni-rich oxide cathodes
- Reduce cost and toxicity ⇒ Mn-rich rather than Co, Ni-rich oxide cathodes
- Reduce/Eliminate Safety Hazard
  - Control electrochemical and chemical reactions to eliminate the risks of thermal runaway
    ⇒ Mn-rich rather than Co, Ni-rich oxide cathodes
    ⇒ Non-flammable electrolytes
    ⇒ Voltage control
Recent Trends

- Demand for Li-ion batteries is increasing dramatically
- Competition for world’s mineral reserves of battery materials is intensifying
  - Anodes: Li, Ti, C (natural graphite)
  - Cathodes: Co, Ni, Mn
  - Electrolytes: F (e.g., LiPF$_6$ salt)
  - Current collectors: Cu, Al
- Ni-rich cathodes (NCA, NMC – 811 and 622) are in vogue (power)
  - Safety concern
  - Cost concern (Co, Ni, Li)
- Mn-rich cathodes still provide an exploitable opportunity
Li- and Mn-rich Composite Electrode Structures (M=Mn, Ni, Co)

- Electrodes comprised of ‘active’ LiMO₂ and ‘inactive’ Li₂MnO₃ components
- Gen 1 cathodes commercialized (160-170 mAh/g)
- Gen 2 cathodes provide 240-300 mAh/g, if activated at 4.6V
High Capacity Li- and Mn-rich Cathodes

The Voltage Fade Limitation

\[ \text{Li/0.5Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25}\text{O}_2 \text{ Cell} \]

- 250 mAh/g
- Voltage decays if cells are charged to high potential, reducing energy output
- Voltage fade attributed to structural instability
Stabilization of High Capacity Cathodes

- Embed transition metal pillars (spinel) to stabilize structures

- **Prime motivation:** Design Mn-rich electrodes that can compete with ‘in vogue’ Ni-rich compositions, e.g., NMC - 811 and 622, to reduce cost and safety concerns
Electrodes containing 5-10% spinel (targeted amount) show significantly improved capacity and rate capability.

Stable cycling at relatively low rate (power).

Croy, Shin et al., J. Power Sources (2016)
Comparison of a Commercial Ni-rich ‘532’ NMC Electrode with a Mn-rich ‘532’ MNC Electrode

A Mn-rich ‘532’ MNC electrode outperforms cells with a commercial Ni-rich ‘532’ NMC electrode at a low current rate.
Mineral Resources in Southern Africa: Li-Ion Batteries

- **Cathodes:**
  - Mn – South Africa (80% of world reserves)
  - Ni – South Africa, Botswana
  - Co – Democratic Republic of the Congo, Zambia

- **Anodes:**
  - C (natural graphite) – Madagascar, Namibia
  - Li – Zimbabwe, Namibia (small, relative to world resources)
  - Ti – South Africa

- **Electrolytes:** F (e.g., LiPF$_6$ salt) – South Africa

- **Current collectors:**
  - Cu – Zambia, South Africa
  - Al – South Africa, Mozambique

⇒ *Major opportunity for materials beneficiation in South and Southern Africa*
⇒ *Need for partnerships to gather know-how and accelerate production*
⇒ *Time is of the essence*
“Energy storage solutions critical for the nation”  
-- Naledi Pandor

- Plant to manufacture precursor materials for Li-ion cathodes launched in Mpumulanga on 10 October 2017
- Focus on manganese based materials – LMO and NMC
- Builds on expertise and competence of past Delta EMD employees

“Beneficiation of raw Mn ore into lithium-ion battery precursor materials will add value of at least twenty fold” – Danie Theron

- It’s never too late to innovate, no matter how inexperienced you are
- Opportunities to innovate:
  - Processing techniques to produce high quality products reproducibly
  - Improved electrode and electrolyte materials’ design
Acknowledgments

Support from the Office of Vehicle Technologies of the US Department of Energy is gratefully acknowledged.