Zinc-air batteries as electric energy storage technology for electric vehicles

SEKUNDÁRNÍ BATERIE ZINEK-VZDUCH JAKO ULOŽIŠTĚ ENERGIE PRO MOBILNÍ APLIKACE

Jaromír Pocedič
Outline

- Energy storage – short recapitulation
- Energy systems for vehicles
- Batteries
- Batteries for electric vehicles
  - State-off art technologies
  - Metal-air batteries
    - Lithium-air
    - Zinc-air
  - Economic assessment
- Research and development of Zn-air technology at laboratory of energy storage
  - Secondary zinc-air battery
  - Power assistant systems
  - Zinc-air for stationary energy storage
Electric energy is all around us

Leads to demand for the energy storage solutions for wide range of applications

Storage of energy for on-demand use
- mobile
- stationary
- **Principles**
  - Chemical
  - Biological
  - Electrochemical
  - Electrical
  - Mechanical
  - Thermal

- **Power (W) vs. Energy (Wh)**
Energy sources for vehicles

- **Combustion engine**
  - Spark- and compression-ignition
  - Fuels:
    - Gasoline, oil
    - LPG, CNG
    - Alcohols (MeOH, EtOH)
    - Biofuels (bio-butanol, bio-oil, bio-EtOH, bio-gas)
    - Hydrogen

- **Electric engine**
  - Energy source
    - Batteries – only energy storage (nuclear, coal, water, wind, sun…)
    - Fuel cells – hydrogen, EtOH, MeOH
    - Ultracapacitor
assumption: driving range of 15000 km/year

Gasoline
- Efficiency 21%, 6L/100km, 1L == 9kWh → 8.1 MWh year

LPG, CNG
- Interesting alternatives, cost competitive, unfortunately non-renewable and often from unstable regions

Biofuels
- 1 generation – production 11.1 MWh/hectare → one car == 0.74 hectare; 500 000 cars in CZ – 17% of the arable land
- 2 generation (biomass) – better convert to heat, biofuel can replace oil in case of step increase in prices
- Algae – high process cost (drying), alternative – production of biogas
Comparison

- **Hydrogen**
  - Development is postponed
  - High prices of catalyst (for $H^+$ fuel cells)
  - Degradation of membranes in fuel cells ($H^+$. For $OH^-$ there is not successful candidate)
  - Safety issues – explosion
  - Overall efficiency around 25%
  - Missing infrastructure
  - Hydrogen corrosion of the high-pressure vessels
  - 95% of hydrogen is produced from fossil fuels

Honda FCX Clarity, California
Electric energy from batteries

- Existing infrastructure
- No at site emissions
- Energy recuperation
- Hybrids are already available in market
- Intensive deployment of EVs to markets
  - Intensive research and development
  - Numerous prototypes and planned models
  - Low sales (Japan, California)
- Main issue - batteries
  - Price of stacks, cycle life
  - Driving range
  - Charging speed

Lexus LS600h - hybrid
Fisker Karma - hybrid
Nissan Leaf – full EV
BATTERIES
Based on electrochemical phenomena
Transformation of chemical energy to electrical and vice versa

History
- “Bagdad” battery
- Luigi Galvani (1780) – A(metal) – frog leg – B(metal)
- Alessandro Volta (1792) – Galvani cell – later battery (50 V, 32 cells)
- Daniel Cell (1836) – Zn-Cu cell
- 19th century – dry cells
Battery principle

- Often two half cells with different chemistry (except concentration cells)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrode reaction</th>
<th>$E^0/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>$Au^{3+} + 3e^- \rightleftharpoons Au$</td>
<td>+1.43</td>
</tr>
<tr>
<td>Ag</td>
<td>$Ag^+ + e^- \rightleftharpoons Ag$</td>
<td>+0.80</td>
</tr>
<tr>
<td>Cu</td>
<td>$Cu^{2+} + 2e^- \rightleftharpoons Cu$</td>
<td>+0.34</td>
</tr>
<tr>
<td>H</td>
<td>$H^+ + e^- \rightleftharpoons H$</td>
<td>0</td>
</tr>
<tr>
<td>Pb</td>
<td>$Pb^{2+} + 2e^- \rightleftharpoons Pb$</td>
<td>-0.13</td>
</tr>
<tr>
<td>Sn</td>
<td>$Sn^{2+} + 2e^- \rightleftharpoons Sn$</td>
<td>-0.14</td>
</tr>
<tr>
<td>Ni</td>
<td>$Ni^{2+} + 2e^- \rightleftharpoons Ni$</td>
<td>-0.25</td>
</tr>
<tr>
<td>Cd</td>
<td>$Cd^{2+} + 2e^- \rightleftharpoons Cd$</td>
<td>-0.40</td>
</tr>
<tr>
<td>Fe</td>
<td>$Fe^{2+} + 2e^- \rightleftharpoons Fe$</td>
<td>-0.44</td>
</tr>
<tr>
<td>Zn</td>
<td>$Zn^{2+} + 2e^- \rightleftharpoons Zn$</td>
<td>-0.76</td>
</tr>
<tr>
<td>Ti</td>
<td>$Ti^{2+} + 2e^- \rightleftharpoons Ti$</td>
<td>-1.63</td>
</tr>
<tr>
<td>Al</td>
<td>$Al^{3+} + 3e^- \rightleftharpoons Al$</td>
<td>-1.66</td>
</tr>
<tr>
<td>Mg</td>
<td>$Mg^{2+} + 2e^- \rightleftharpoons Mg$</td>
<td>-2.37</td>
</tr>
<tr>
<td>Na</td>
<td>$Na^+ + e^- \rightleftharpoons Na$</td>
<td>-2.71</td>
</tr>
<tr>
<td>K</td>
<td>$K^+ + e^- \rightleftharpoons K$</td>
<td>-2.93</td>
</tr>
<tr>
<td>Li</td>
<td>$Li^+ + e^- \rightleftharpoons Li$</td>
<td>-3.05</td>
</tr>
</tbody>
</table>
Primary batteries
- One time use
- High capacity
- Chemistry
  - Zinc-Carbon (1.5 V)
  - Zinc-MnO₂ (1.5 V)
  - Lithium (3.0 V)
  - Zinc-air (1.35-1.65 V)

Secondary batteries
- Rechargeable
- Lower capacity
- Chemistry
  - Nickel-Cadmium (NiCd)
  - Lead-Acid
  - Nickel-Metal Hydride (NiMH)
  - Nickel-Zinc (NiZn)
  - Lithium-Ion (Li-ion)

Flow batteries
- One of redox pairs in form of solution
- All-vanadium
- Iron-Chromium
- Cerium-Zinc
BATTERIES FOR ELECTRIC VEHICLES
Batteries for electric vehicles

- Parameters of batteries
  - Fast charging
  - Safety
  - High specific capacity
  - High specific power or power assistant system

- Art of state technologies
  - Advanced lead-acid
  - Nickel-metalhydride (NiMH)
  - Lithium-ion (Li-Ion)
  - Zebra Na-NiCl₂ (NaAlCl₄)

- Promising technologies: Metal-air systems
Lead-acid and Nickel-metalhydride

- **Lead-acid**
  - 30-40 Wh/kg; 180 W/Kg
  - Efficiency 50-90 %
  - Cycle life – 500-800
  - Voltage – 2.1 V
  - Price – 100-200$/kWh
  - Adv. lead acid (48 Wh/kg)
  - Heavy batteries, low cost

- **Nickel-metalhydride**
  - 60-80 Wh/kg; >200 W/Kg
  - Efficiency 60 – 70 %
  - Cycle life – 500-1000
  - Voltage – 1.2 V
  - Price – 800-1000$/kWh
  - Rare metals needed
Lithium ion

- 100-200 Wh/kg; 250-340 W/Kg
- Efficiency 80-90%
- Cycle life – 400-4000
- Voltage – 3.6 V
- Practical spec. energy in cars around 130 Wh/kg
- Price - >400$/kWh estimation

- Safety issues
- Lithium scarcity and unstable sources
- **Nissan Leaf**
  - 24 kWh lithium ion
  - Driving range
    - 117 km (73 mi) (EPA)
    - 175 km (109 mi) (NEDC)
    - 76 to 169 km (47 to 105 mi) (Nissan)

- **Renault Zoe**
  - 22 kWh lithium ion
  - Driving range
    - 210 km (130 mi) (NEDC)
Other technologies

- **Zebra battery**
  - Na-NiCl2
  - 120 Wh/kg
  - 680$/kWh
  - >250°C

- **Ultracapacitors**
  - EC double-layer or pseudo-capacitors
  - 5-10 Wh/kg
  - 2000$/kWh
  - New low cost UC on the way (150$/kWh)
Metal-air batteries

- Increased research in this area
- Unlimited source of reactants at positive electrode (air) ➞ high specific capacity
- Primary and secondary batteries, fuel cells
- Li, Na, Ca and Mg needs non-water electrolyte

<table>
<thead>
<tr>
<th>Metal/air battery</th>
<th>Calculated OCV, V</th>
<th>Theoretical specific energy, Wh/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Incl. oxygen</td>
</tr>
<tr>
<td>Li/O₂</td>
<td>2.91</td>
<td>5200</td>
</tr>
<tr>
<td>Na/O₂</td>
<td>1.94</td>
<td>1677</td>
</tr>
<tr>
<td>Ca/O₂</td>
<td>3.12</td>
<td>2990</td>
</tr>
<tr>
<td>Mg/O₂</td>
<td>2.93</td>
<td>2789</td>
</tr>
<tr>
<td>Zn/O₂</td>
<td>1.65</td>
<td>1090</td>
</tr>
</tbody>
</table>
Advantages
- High specific capacity
- Linear discharge curve
- Low self-discharge
- Non-toxic
- Low price of base materials (except Li)

Disadvantages
- Influence of environment conditions (temperature, humidity, pressure, $O_2$ and $CO_2$ concentration)
- Drying at air
- The power of the battery is limited by reactions at positive (air) electrode
Lithium-air battery

\[
\text{Li}^{(s)} \rightarrow \text{Li}^+ + \text{e}^-
\]

(negative electrode)

\[
\text{Li}^+ + \frac{1}{2}\text{O}_2 + \text{e}^- \rightarrow \frac{1}{2}\text{Li}_2\text{O}_2
\]

(positive electrode)

\[
\text{Li}^+ + \text{e}^- + \frac{1}{4}\text{O}_2 \rightarrow \frac{1}{2}\text{Li}_2\text{O}
\]

(positive electrode)
Zinc-air battery

- Primary battery form 80s 19th century
- Attempts to make secondary batteries begins at same time

In alkaline solution

Anode: $\text{Zn(OH)}_4^{2-} + 2e^- \leftrightarrow \text{Zn} + 4\text{OH}^-(aq)$

Cathode: $\text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \leftrightarrow 4\text{OH}^-(aq)$

Potential:
- $E^{\circ} = -1.25$
- $E_1 < 1.65$ (discharge)
- $E_2 > 1.65$ (charge)
- $E_{eq} = 1.65$
- $E^{\circ} = 0.4$

Overpotential for ORR

Chemical reactions:
- $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
- $2\text{Zn}^{2+} + 4\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-}$
- $[\text{Zn(OH)}_4]^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^-$

- $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$
- $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$
# Li-air vs. Zn-air

<table>
<thead>
<tr>
<th>Zinc - air</th>
<th>Lithium - air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable at contact with water</td>
<td>Instability with water, increases manufacturing costs</td>
</tr>
<tr>
<td>Cheap raw materials</td>
<td>High costs of lithium and no aqueous electrolytes</td>
</tr>
<tr>
<td>Known technology (primary), already exists some companies with systems near realization</td>
<td>At stage of fundamental research</td>
</tr>
<tr>
<td>Bad reversibility of Zn electrode, high over potentials at air electrode</td>
<td>Good reversibility</td>
</tr>
<tr>
<td>Low voltage of cell</td>
<td>High voltage of cell</td>
</tr>
<tr>
<td>1300 Wh/kg</td>
<td>Up to 11000 Wh/kg</td>
</tr>
</tbody>
</table>

- Chosen zinc-air
- Some components and know-how is transferable to another metal-air systems in the future
Battery economy balance

- **Economy balance**
  - Driving range - 8km per kWh (4.5 – 9 by GM)
  - Drive train efficiency 75%, charging efficiency 90%
  - 100km → approx. 18 kWh → 90 CZK (5 CZK/kWh)
  - Gasoline: 6L/100 → 210 CZK/100 km
  - Difference == price of battery == 6.7 CZK/kWh/cycle
  - Battery with life-time 500 cycles (2 years of service) should cost 3350 CZK/kWh == **135 EUR/kWh**

- **Lithium vs. Zinc sources**
  - Zinc: 30kWh battery == 60 kg of Zinc → for 12mil. of EV we need 5.8% of the annual Zn production
  - Lithium: 30kWh battery == 11.6 kg of Li → for 12mil. of EV we need 410% of the annual Li production
### Battery economy

- **Comparison of the battery parameters**

<table>
<thead>
<tr>
<th></th>
<th>Cycle life</th>
<th>price ($/kWh)</th>
<th>energy density (kWh/kg)</th>
<th>efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-ion</td>
<td>400-4000</td>
<td>&gt;400 (2000)</td>
<td>100-200</td>
<td>80-90</td>
</tr>
<tr>
<td>NiMH</td>
<td>500-1000</td>
<td>800-1000</td>
<td>60-80</td>
<td>60-70</td>
</tr>
<tr>
<td>Lead-acid</td>
<td>500-800</td>
<td>120</td>
<td>30-40</td>
<td>50-90</td>
</tr>
<tr>
<td>Ultracap.</td>
<td>&gt;20000</td>
<td>4000</td>
<td>5-10</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Zinc-Air</td>
<td>300</td>
<td>60-130</td>
<td>150-250</td>
<td>60-70</td>
</tr>
<tr>
<td>Zebra</td>
<td>&gt;1000</td>
<td>680</td>
<td>120</td>
<td>50-80</td>
</tr>
</tbody>
</table>

Need to be increased to 500 cycles
RESEARCH OF SOLUTIONS FOR EV
LABORATORY OF ENERGY STORAGE
UWB-NTC/ICT Prague

Zinc-air energy storage systems
Power assistant technology for EVs
Zinc-air development in LES

- **Secondary battery**
  - Zinc as solid negative electrode
  - Air electrode with bifunctional catalyst
  - For mobile applications

- **Zinc-air fuel cell**
  - Zinc in form of suspension or plates
  - Recharge
    - Mechanical – plates, suspension
    - Electrochemical – suspension
  - Air electrode specialized for OER or ORR
  - For mobile and stationary applications
  - For stationary – can be used for long term storage and as capacity extender
Zinc-air development in LES

- **Zinc electrode**
  - Intensive research of zinc electrode structure for both zinc-air technologies
  - additives
  - electrolytes
Zinc-air development in LES

- **Air electrode**
  - Different structures
  - Catalysts screening
  - Catalyst deposition methods

- **Diagram**
  - Hot pressed catalyst layer
  - Air-brush catalyst layer
  - Electrospayed catalyst layer
  - Electrode without catalyst

- **Graph**
  - Current vs. Potential vs. Hg/HgO (V)

- **Image**
  - SEM images of different catalyst layers
Power assistant systems for Zinc-air battery

- Electrospray technique for preparation of metal-oxide nano-layers ($\text{MnO}_2$, $\text{TiO}_2$, $\text{Co}_3\text{O}_4$)
- Pseudocapacitors
  - $\text{MnO}_2$ – cheap
- Lithium – ion batteries
  - $\text{Li}_x\text{Ti}_y\text{O}_z$

Faradaic behavior

![Graph showing current and voltage vs. SHE](image)

![Electrospray setup](image)
Milestones in Zinc-air development

- What's needed to solve for successful commercialization
  - High over potentials for OER and ORR
  - Search for catalyst
  - Structure modification for better mass transfer of reactants
  - Parasitic reactions at negative electrode (hydrogen evolution)
  - Electrolyte additives and electrode surface modifications
  - Change of the zinc morphology during charge/discharge
  - Zinc electrode isolation by ZnO
Future

- Laboratory units
  - Done – secondary battery, electrode testing systems
  - In progress – zinc-air fuel cell, zinc regeneration system
- Pilot units for EV and stationary energy storage
- Combined battery and power assistant system unit
- Application tests – “far future”
  - Small electric vehicle
    - wheelchair
    - Golf cart
    - Electro bike
  - Unit for EV
    - Battery
    - Power assistant system
Thanks for your attention

Juraj Kosek

Jan Dundálek, Jožka Chmelař, Ivo Šnajdr