Energy

how much potential a physical system has to change. In physics, energy is a property of matter and space, objects and fields.
Conservation of Energy

Energy can be transferred between objects and can also be converted in form. It cannot, however, be created or destroyed (conservation of energy).

Electricity → light

Fuel → movement

Movement → electricity → light
Energy Required

- 28% increase in energy from 2015 to 2040

Climate Change

Robert Rhode

https://www.youtube.com/watch?v=xWpTGbZhZfQ
CO₂ Temperature Scenarios

Source: IPCC, AR5, 2014 & Bob van der Zwaan (TNO-ECN/UvA)
Sustainable Energy

For example Sun:

- Sun: **9000x** the required energy
- Intermittent availability → **STORE**
- Not all energy is easy “to catch”
BATTERIES
Most stable configuration: filled outer shell
Electrochemical/Galvanic Cell Cu-Zn

Redox reactions

Reduction: \( \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu(s)} \) + 0.34 V

Oxidation: \( \text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \) + 0.76 V

\( \text{Cu}^{2+} + \text{Zn(s)} \rightarrow \text{Zn}^{2+} + \text{Cu(s)} \)
Battery

A dry cell battery releases electricity through a chemical reaction that takes place between the zinc alloy outer can (the anode)...

A porous cardboard separator keeps cathode and anode apart.

When a circuit is closed, current flows through the battery. It can move in either direction, depending upon circuit design and conductive material.

...and an electrolyte paste inside the battery (the cathode).

The electricity is conducted through a carbon rod in the center of the battery.
Lead Acid Battery

- Low volumetric and gravimetric capacity
- Sulfuric acid, lead....
- But, high surge current and large power-to-weight ratio
- Low cost

Car battery

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NiFe Battery (Edison)

- Cheap
- Low efficiency of charge
- H₂ gas formation in side-reaction

\[
2 \text{NiO(OH)} + 2 \text{H}_2\text{O} + 2 \text{e}^- \leftrightarrow 2 \text{Ni(OH)}_2 + 2 \text{OH}^-
\]

\[
\text{Fe} + 2 \text{OH}^- \leftrightarrow \text{Fe(OH)}_2 + 2 \text{e}^-
\]

Jungner, E. W. Swedish patent no. 10177, 1899.
Edison, T. A. Reversible Galvanic Battery. US patent no. 692,507, 1902.
The Nobel Prize in Chemistry 2019 was awarded jointly to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino "for the development of lithium-ion batteries."
Periodic Table and Lithium

- **Lightest metal with density 0.53 g/cm³**
- **Low standard reduction potential Li⁺/Li = -3.05 V vs SHE**
  → High density, high voltage battery

Very reactive with oxygen, air and water!
→ Water and oxygen free system and solvent
Li ion Battery

- Lithium anode → cathode should be able to incorporate Li⁺ ions

(1) large, constant intercalation free energy change
(2) accommodate the guest ion with minimal structural change
(3) high diffusivity of the alkali ion within the structure
(4) allow the intercalation reaction to proceed reversibly
(5) display good electronic conductivity
(6) be insoluble in the electrolyte, no co-intercalation of electrolyte components
(7) operate under close to ambient conditions.
Whittingham (~1976)

$\text{Li}_x\text{TiS}_2 \ (0 \leq x \leq 1)$

Goodenough (~1980)

Oxygen small electronegative element: cation uptake large negative free energy change and high cell voltage: 4-5 V
Lithium Anode

- Whiskers and/or dendrites → short-circuit
- ‘Dead’ lithium – no longer available for EC

In situ X-ray tomography observation of lithium dendrites: (a) schematics of an in situ cell (Eastwood et al.), reproduced from ref. 20.
Anode material: Intercalation Li not easy, (carboneceous) material not stable $\rightarrow$ Petroleum coke stable; mixture of crystalline and non-crystalline coke
4.2 V; 400 Wh/l
Cathode Development

Oxide of choice:

NMC – Ni, Mn, Co oxide

Anode

per 1gm Graphite (LiC₆)

= 26.8/(12*6) Ah/g

= 0.370 Ah/g
LCO / Graphite Battery
Battery Build-up

- Metal Foil - Current Collector
- Cathode
- Separator
- Anode
- Metal Foil - Current Collector
WHAT IS NEXT?
Safety

- Li dendrites/Whiskers
- Electrolyte stability

https://www.youtube.com/watch?v=SMy2_qNO2Y0
start and after 1.50 minutes
Electrolytes

- Dimethyl carbonate
- Ethylene carbonate
- Propylene carbonate

Graph showing voltage versus lithium (V vs. Li) with different electrolyte regions:
- Ether 0~3.5 V
- Esters 1.0~4.1 V

Chemical structures and labels:
- GR
- Li
- SEI
- CEI
- Expanded window due to kinetic protection ~5.0 V
- SHE
- LFP
- LCO
- NMC
- LMNO
- LCP
Stability Li Ion Batteries

Dissolution metal ions?
Penlite (AA)
Energy = 5Wh = 18 kJ

4 batteries
21 Wh = 76 kJ

55 batteries
2000 – 2500 kcal
1000 kJ

Huishouden (4 personen)
8 miljoen batteries per day
55 biljoen \((10^{12})\) Joules per year

100 km
3200 AA batteries
16 kWh = 57600 kJ
1 l / 56 km!

8 miljoen batteries per day
55 biljoen \((10^{12})\) Joules per year

60 biljoen \((10^{12})\) batteries
1075 peta \((10^{15})\) Joules per year
Volumetric and Gravimetric Capacity

- Store large amounts of energy
- Weight or volume important?

- $5 \text{ Wh} = 18 \text{ kJ}$
- $20 \text{ kWh} = 72 \times 10^6 \text{ J}$
- $100 \text{ kWh} = 360 \times 10^6 \text{ J}$
Capacity – Electric Cars

* Projected metrics for current Lithium Ion Battery and BEV Technology:
  
  - 200 Wh/kg\(_{\text{battery}}\)\(^{[1]}\)
  - 95% discharge efficiency
  - 80% state-of-charge range
  - 250 €/kWh\(_{\text{battery}}\) (2030 estimate)\(^{[2]}\)
  - 100 Wh/km (4-passenger car)

<table>
<thead>
<tr>
<th></th>
<th>150 km range</th>
<th>500 km range</th>
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<tbody>
<tr>
<td>Required energy</td>
<td>20 kWh(_{\text{battery}})</td>
<td>66 kWh(_{\text{battery}})</td>
</tr>
<tr>
<td>Battery weight</td>
<td>100 kg</td>
<td>330 kg</td>
</tr>
<tr>
<td>Battery cost</td>
<td>5000 €</td>
<td>16500 €</td>
</tr>
</tbody>
</table>

- Current technology only feasible for short-range BEVs
  → Range anxiety may limit market-penetration

- Additional issues like safety, deactivation, etc.
- Similar problems stationary storage

2. Transition to Alternative Transportation Technologies – PHEV, National Research Council (2010)
Capacity Compared

Liquid $\rightarrow$ solid electrolytes
Lithium ions $\rightarrow$ Lithium metal
Battery Processes

Cell Chemical Reaction Times

Electrolyte

- Ion Flow
- Mass transport / Diffusion region
  - T>several hours

Electrode

- Intercalation region
  - T>several hours

Charge transfer region
- T<1 minute

Charge transfer / chemical conversion at the electrode surface (Short time constant)

Mass transfer / diffusion of ions in the electrolyte bulk
- (Long time constant. Continues until all materials have been transformed or transferred)

Intercalation of ions in the electrode bulk (Long time constant)
1896
Rontgen Nobel Prize 1901

Museum Boerhave, 2015
Stability Li Ion Batteries

- LP57, 7.1 mg\(_{\text{NMC}}\)/cm\(^2\)
- LP572, 7.1 mg\(_{\text{NMC}}\)/cm\(^2\)

Dissolution metal ions?

<table>
<thead>
<tr>
<th>Spec. Discharge Capacity [mAh/g(_{\text{NMC}})]</th>
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<tbody>
<tr>
<td>240 - 180</td>
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<tr>
<td>160 - 120</td>
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<tr>
<td>140 - 100</td>
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<tr>
<td>120 - 80</td>
</tr>
<tr>
<td>80 - 40</td>
</tr>
<tr>
<td>40 - 0</td>
</tr>
</tbody>
</table>

- 3.0 V - 4.3 V
  - 0.1C, 0.2C, 0.5C, 1C, 2C, 3C, 4C, 5C, 10C, 50 cycles 1C
  - Charge: CCCV max. 1C, Discharge: CC

- 3.0 V - 4.5 V
  - 0.5C, 1C, 2C, 10C
  - Charge: CCCV max, 1C
  - Charge: CCCV, Discharge: CC

- 3.0 V - 4.3 V
  - 50 cycles, 1C
  - Charge: CCCV
  - Discharge: CC

- Loss: 2.0777 mAh/g, 1.3 %
- Loss: 4.0947 mAh/g, 2.6 %
Li-ion Deactivation: Metal Dissolution

- Dissolution of TM (and accumulation on graphite anode) \(\rightarrow\) no longer available for EC
- Compare 'dead' Li

Challenges: Self-Discharge

**LiS battery**
- Dissolution $S_8$
- Migration of sulfur through cell
- Formation of polysulfides $S_x^{2-}$
LiS Battery: Discharge

\[ F_{\text{red}} = F_{\Sigma S}^{2500 \text{ eV}} - F_{\Sigma S}^{2475.5 \text{ eV}} \]

- \( F_{\text{red}} << 0 \): Li\(_2\)S (blue)
- \( F_{\text{red}} >> 0 \): S\(_8\) (red)
- \( F_{\text{red}} \sim 0 \): S\(_x^{2-}\) (white)

Formation inaccessible Li\(_2\)S at counterelectrode

LiS Cycling

- Lithiated nafion membrane

\[ F_{\text{red}} = F_\Sigma S_{2500 \text{ eV}} - F_\Sigma S_{2475.5 \text{ eV}} \]

- \( F_{\text{red}} \ll 0: \text{Li}_2\text{S (blue)} \)
- \( F_{\text{red}} \gg 0: \text{S}_8 \text{ (red)} \)
- \( F_{\text{red}} \sim 0: \text{S}_x^{2-} \text{ (white)} \)

Rare Element Availability

Lithium, Cobalt and graphite

Lithium availability? Lithium extraction from brine and minerals

Cobalt is mined in the Democratic Republic of Congo (slave and child labor) and political situation is unstable

OTHER BATTERY CHEMISTRIES?
Recycling E-waste

Not easy
Safety aspects
Energy and costs associated
Lots to be done!
Projected Demands and Costs
Projections Mobility

TIAM-ECN calculation of the distance travelled in 2050 by type of energy carrier for passenger cars in Europe under stringent climate policy and 100$/bl oil prices with varying assumptions for the cost of batteries.
Queen opens electrical cracker

Yesterday, Queen Anneke switched on the third electrical cracker in the renovated chemical complex in Rotterdam. The Queen pressed the “on”-button as announced in 2008. This national initiative for the development and scaling up of electrolysis was reactivated.

A group of Dutch chemists have developed batteries that contain just water and carbon and that make use of air. These are more environmentally friendly, safer and cheaper than nowadays batteries. The battery is ready for the mobile future: regenerate your cellphone in 20 minutes.

These batteries are expected to enable the widespread use of water-electric batteries that many people have at home to store electricity from solar panels. A low-cost, polarized battery, which is still in the development of the mobile小女孩, has already demonstrated that the new batteries work just as well as those from the battery and have a longer lifespan, are also efficient and also safe.

Professor of sustainable energy storage Maarten Tiemers, who has collaborated with the University of Groningen, has created a new battery that is more environmentally friendly and has a higher energy density. This battery is expected to be much cheaper than existing batteries. The team is currently working on a new battery that can be charged in just a few minutes.

Cars and mobile phones

The battery is currently not yet suitable for use in mobile equipment. The design for the car battery is in the test stage and will be compact and also safe. The battery is also compatible with use in other devices. The energy storage of the battery is currently under development.

Dutch chemists create breakthrough

A GENUINLY CLEAN AND CHEAP BATTERY

GROWNING - Environmentally friendly, safe and affordable batteries pave the way for a cleaner electric vehicle. This technology was developed at the end of 2016 and is now ready for use in real-life situations. The technology is based on a chemical reaction between carbon dioxide and water. The advantage of this technology is that it can be charged in a few minutes and that it can be used in a wide range of applications. The battery is expected to be much cheaper than existing batteries and will also be safer.

Capital injection

The battery has received a large order for the initial principal batteries and that made it possible to further develop the environmentally friendly batteries. The new batteries provide more storage capacity for the larger Dutch offshore wind parks. “The system is simple and efficient,” said Dr. Tiemers. The technology will be tested in a real-life situation in 2018. The battery is also compatible with use in other devices.
Energy Storage