Electrochemical Reduction of CO$_2$
Power to Value

Compound based Energy Storage

Overcapacity of Renewable Electricity

CO₂ from fossil-fired power plants

Energy + CO₂

Electrocatalysis

Synthetic fuels or chemical feedstock

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Market Price</th>
<th>Market Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH₄)</td>
<td>81 €/t</td>
<td>&gt; 2400 Mt/y</td>
</tr>
<tr>
<td>Ethylene (C₂H₄)</td>
<td>1000 €/t</td>
<td>141 Mt/y</td>
</tr>
<tr>
<td>Formic acid (HCOOH)</td>
<td>650 €/t (+ H₂ ⇄ Naphtha)</td>
<td>&gt; 210 000 Mt/y</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Remarks: Power-to-Gas
The Ideas behind CO$_2$-to-Value

**Heat of combustion**

\[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad + \quad 286 \text{ kJ} \]

\[ CH_4 + 3 O_2 \rightarrow 2 H_2O + CO_2 \quad + \quad 890 \text{ kJ} \]

Combustion stability of the net 2%

- max. H$_2$ addition/perfect mixing 2.9%
  - (price increase for customer)
  - (not 8% as technical feasible)

Energy storage with H$_2$ reduction is very attractive from energetic considerations, but low attractive from economic considerations

⇒ What can we do with electrochemistry to overcome such problems
Complexity Analysis
Direct catalytic reduction of CO₂

Vision
Photocatalysis
• diluted CO₂ (350 ppm)
• Protons from water
• Electrons from oxygen
• presence of O₂ (air)
• all energy from photons
• enrichment, separation, collection in one unit
• distributed and not stationary
• autarkic

Simplification
• conc. CO₂ (20 – 100 %)
  (up to 50000 t/day/plant)
• H₂ as such
• inert (no competitive back - reaction)
• energy from photons & electro-assistance
• stationary
• separation of products & educts can be solved (process flow)

Photo catalytic Reaction Center
• all on one micro particle
  very complex
• CO₂-reduction catalyst
• H₂O/CO₂-oxidation catalyst
• (add O₂ non-sensitivity)
• photo-sensitizer dye
• catalysts for consecutive reactions @ high temp.
• Keys
  energy-level alignment yield

Electro assisted Photo-catalysis & electro catalysis
• published photo anodes & cathodes relay on photo assistance
• reduction & oxidation catalyst separated
• electrolyte determines products & yield
• highest projected efficiency
• Intermediate business case?
  CO₂- Electrolyzer (I)
  Energy Storage
  Carbon Capture (E)
CO₂-Electrolyser – basic principle

Carbon dioxide (CO₂)

- 34,032 million tons carbon dioxide (CO₂) were emitted for energetic usage in 2011
- F.e. Germany’s biggest power station Niederlaussem emitted 26 million tons in 2011

Renewable electricity

- Excess energy of 10 TWh can be expected

Electrolyzer

- High Faradic Efficiencies
  - Current Eff. > 90%
- Low power consumption
  - System Eff. > 50%
- High turnover rates
  - current densities > 0.3A/cm²
- Long lifetime
  - > 4000h

Possible Products

- Ethylene (C₂H₄)
- Carbon monoxide (CO)
- Methane (CH₄)
- Formic acid (HCOOH)
- Methanol (CH₃OH)
- Ethanol (C₂H₅OH)

Separated by post combustion carbon capture process

Dependent on catalyst
CO₂ reduction on metal electrodes in aqueous solution

<table>
<thead>
<tr>
<th>Electrode</th>
<th>CH₄</th>
<th>C₂H₄</th>
<th>C₂H₅OH</th>
<th>C₃H₇OH</th>
<th>CO</th>
<th>HCOO⁻</th>
<th>H₂</th>
<th>Total</th>
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<td>Cu</td>
<td>33.3</td>
<td>25.5</td>
<td>5.7</td>
<td>3.0</td>
<td>1.3</td>
<td>9.4</td>
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<tr>
<td>Au</td>
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<td>0.0</td>
<td>0.0</td>
<td>87.1</td>
<td>0.7</td>
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<td>6.1</td>
<td>9.9</td>
<td>95.4</td>
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<td>99.5</td>
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<tr>
<td>In</td>
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<td>0.0</td>
<td>0.0</td>
<td>2.1</td>
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<td>7.1</td>
<td>88.4</td>
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<td>100.1</td>
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<td>Cd</td>
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<td>0.0</td>
<td>0.0</td>
<td>13.9</td>
<td>78.4</td>
<td>9.4</td>
<td>103.0</td>
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<tr>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>95.1</td>
<td>6.2</td>
<td>101.3</td>
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<tr>
<td>Ni</td>
<td>1.8</td>
<td>0.1</td>
<td>0.0</td>
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<td>0.0</td>
<td>1.4</td>
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<td>0.0</td>
<td>94.8</td>
<td>94.8</td>
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<tr>
<td>Pt</td>
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<td>0.0</td>
<td>0.1</td>
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<td>Ti</td>
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<td>0.0</td>
<td>0.0</td>
<td>99.7</td>
<td>99.7</td>
</tr>
</tbody>
</table>


- CO₂ can be reduced at metal electrodes in aqueous solution
- Copper leads to a variety of different hydrocarbons
- For some metals hydrogen evolution is dominating in aqueous media
Electrochemical Conversion of CO₂
Basic Considerations - economic

**Ethylene: Single Step Process - 1 electrochemical**

2 CO₂ + 2 H₂O → 3 CO + C₂H₄

- Anode: Copper electrode
- Cathode: Aqueous electrolyte
- Ethylene ~ 1000€/t

**CO: Three Step Process - 2 electrochemical + 1 thermal**

- Anode: Different electrolytes and electrodes
- Cathode: Different electrolytes and electrodes
- Fischer-Tropsch Verfahren
  - Zn: Methanol
  - Fe: Hydrocarbons
  - i.e. Naphtha (~ 650 €/t)
Electrochemical Conversion of CO$_2$
Basic Considerations - Efficiency

- Efficiency improvement
- Higher current density for unchanged product composition

Goal for 2015

- Lab-scale product feasibility demonstrated, but not on an industrial-relevant level
## Topic of Current Development

### Build up of “high pressure” setup (30 bar)
- The increased pressure leads to an increased concentration of CO\(_2\).
- But also the decreased volume of the reduction products will help to increase current densities.

### Ionic liquids as electrolyte
- IL’s seems to be an ideal alternative to water as electrolyte.
- Higher solubility of CO\(_2\) compared to water.
- Reduction of over potentials (catalytic activity).
- Suppression of H\(_2\)-evolution.

### Electrode development
- Development of a catalyst system of (binary/ternary) electrode & electrolyte system with a stable product composition & long lifetime.

### Gas diffusion Electrodes
- High concentration of gaseous CO\(_2\) at the three-phase interface (gas/solution/solid) should help to increase selectivity of ethylene.
Electrochemical Reduction of CO$_2$ to CO
Siemens flow cell setup

**Anolyte cycle**

- No gasses in the electrolytic chamber (catholyte will be saturated with CO$_2$ before)
- Pressurized system up to several bars
- Peristaltic pump to control Catholyte flow

**Catholyte cycle**

- Peristaltic pump
- Gas separation
- Product exit
- CO$_2$-Saturation

Medium Pressure CO$_2$-Electrolysis

Setup of our current “1 bar” setup

Full SYSTEM includes pumps, gas separation etc. Gas Diffusion Electrode for high current densities
How to increase system efficiency?

\[ U_{\text{total}} = U_{\text{anode}} + U_{\text{electrolyte}} + U_{\text{nafion}} + U_{\text{cathode}} \]

Reduction of IR-drop over electrolyte at high current densities
- Reduced distance between electrodes
- Increased conductivity (increased salt amount, increased temperature)

\[ U_{\text{electrolyte}} = U_{\text{Anolyte}} + U_{\text{Catholyte}} = \left( \rho_{\text{Anolyte}} + \rho_{\text{Catholyte}} \right) \frac{l}{A} \cdot I \]

Reduction of over potential
- By choice of hydrogen ion activity (pH) and salt anion / cation of anolyte and catholyte

\[ E_0 = -1.31 \text{V} \]

Reduction of IR-drop over electrolyte:
- 10 mm to 2.5 mm
- ~10 mS/cm to ~380 mS/cm
Optimization of System Efficiency (chemical approach)

**Current voltage characteristics**

<table>
<thead>
<tr>
<th>Current density / mA cm²</th>
<th>Cell potential / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>@ -3.0 V:</td>
<td></td>
</tr>
<tr>
<td>-7 mA/cm²</td>
<td></td>
</tr>
<tr>
<td>-33 mA/cm²</td>
<td></td>
</tr>
<tr>
<td>-71 mA/cm²</td>
<td></td>
</tr>
<tr>
<td>-88 mA/cm²</td>
<td></td>
</tr>
<tr>
<td>@ -3.0 V:</td>
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<td></td>
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<tr>
<td>-33 mA/cm²</td>
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<tr>
<td>-71 mA/cm²</td>
<td></td>
</tr>
<tr>
<td>-88 mA/cm²</td>
<td></td>
</tr>
</tbody>
</table>

**Catholyte / Anolyte**

- **0.1 M KHCO₃ / 0.1 M KHCO₃**
  - 10 mS/cm / 10 mS/cm
- **0.5 M K₂SO₄ / 2.5 M KOH**
  - 72 mS/cm / 380 mS/cm
- **3.0 M KBr pH3 (H₂SO₄) / 2.5 M KOH**
  - 315 mS/cm / 380 mS/cm
- **4.0 M KBr pH3 (H₂SO₄) / 2.5 M KOH**
  - 379 mS/cm / 380 mS/cm

**Conclusions**

- Current densities can be raised, by increasing electrolyte conductivities (thus decreasing IR Drop)
- For electrical conductivities > 350 mS/cm, the current densities can be increased up to 600 mA/cm²
- For high current densities the I-V-curve gets rippled, due to the occurring high gas evolution at the electrode surfaces and the pulsed electrolyte flow, caused by the diaphragm pump
Toward Industrial Relevant Systems

Current-Voltage characteristics

- By using Gas Diffusion Electrodes the current densities before hydrogen evolution becomes dominating can be increased.
- To increase system efficiency the system voltage was reduced by decreasing electrode distance (10 mm to 2.5 mm), increasing conductivity (10 mS/cm to ~300 mS/cm) and optimizing pH of electrolyte.
- The solubility of CO₂ seems to play no role for the GDE approach.
- Further optimization potential is CO₂ flow through GDE, increased pressure and choice of electrolyte.

Solid electrode (2013)

<table>
<thead>
<tr>
<th>Current Density [mA/cm²]</th>
<th>Current Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FE - H₂</td>
<td>FE - CO</td>
</tr>
<tr>
<td>4.5 mA/cm²</td>
<td>88%</td>
</tr>
<tr>
<td>5.3 cm²</td>
<td>29%</td>
</tr>
</tbody>
</table>

GDE (2014 - no optimum)

<table>
<thead>
<tr>
<th>Current Density [mA/cm²]</th>
<th>Current Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>CO</td>
</tr>
<tr>
<td>48.2 mA/cm²</td>
<td>93%</td>
</tr>
<tr>
<td>9 cm²</td>
<td>49%</td>
</tr>
</tbody>
</table>

U: 4.0 V
J: 4.5 mA/cm²
A: 5.3 cm²
FE: 88%
SE: 29%

U: 2.5 V
J: 48.2 mA/cm²
A: 9 cm²
FE: 93%
SE: 49%
CO₂ reduction to CO at silver cathode

- April 2013: ca. 10V, 5 mA/cm², 9% SE
- September 2013: 4V, 5 mA/cm², 29% SE
- January 2014: 2.5V, 49 mA/cm², 49% SE
- February 2014: 3.25V, 110 mA/cm², 40% SE

- Simple U-tube
- First proof of CO
- Flow cell
- Continuous production
- 2.5mm distance
- Gas diffusion electrode
- Optimized electrolyte
- Optimized gas and electrolyte flow
High pressure electrolysis setup

- Anolyte circle
- Catholyte circle
- Electrolyte reservoir with gas separation
- Electrolysis cell
- WADose - HPLC pump
- mini Cori-Flow - mass flow meter

**CO₂ To Value**
Ionic liquids (IL) saturated with CO$_2$ show a reduction to CO with high Faradic Eff. (~80%) and high Selectivity (nearly 100%) at reduced voltages, no hydrogen evolution was observed.

Test of several ionic liquids showed promising candidates with broad electrochemically stable window.

- Optimization and long term evaluation in progress
Electrochemical Reduction of CO$_2$ to C$_2$H$_4$
CO₂ reduction on copper electrodes


Table 1  Products of CO₂ reduction along with the number of electrons needed to produce each one and its standard reduction potential at pH 6.8. Products shown in green appear in only a few past studies, and products shown in blue are reported here for the first time.

<table>
<thead>
<tr>
<th>Product</th>
<th># e⁻</th>
<th>E</th>
<th>Product</th>
<th># e⁻</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formate</td>
<td>2</td>
<td>-0.02</td>
<td>Acetaldehyde</td>
<td>10</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>2</td>
<td>-0.10</td>
<td>Ethanol</td>
<td>12</td>
<td>0.09</td>
</tr>
<tr>
<td>Methanol</td>
<td>6</td>
<td>0.03</td>
<td>Ethylene</td>
<td>12</td>
<td>0.08</td>
</tr>
<tr>
<td>Ethanol</td>
<td>9</td>
<td>0.01</td>
<td>Glycoxal</td>
<td>14</td>
<td>0.46</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>2</td>
<td>0.15</td>
<td>Methane</td>
<td>16</td>
<td>-0.14</td>
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<tr>
<td>Allyl alcohol</td>
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<td>0.15</td>
<td>Acetaldehyde</td>
<td>16</td>
<td>0.11</td>
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<tr>
<td>Aldehydes</td>
<td>0.1</td>
<td></td>
<td>Acetate</td>
<td>16</td>
<td>0.11</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.5</td>
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<td>Acetate</td>
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<td>Ethylene glycine</td>
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<td>Glycolaldehyde</td>
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<tr>
<td>Hydroxyacetone</td>
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<td></td>
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<td>18</td>
<td>0.21</td>
</tr>
</tbody>
</table>
Ethylene Formation at Copper Based Electrodes

- CO\textsubscript{2} is selectively reduced to C\textsubscript{2}H\textsubscript{4}
- In the beginning no CO\textsubscript{2} reduction can be found
- After 30 min. the maximum FE of C\textsubscript{2}H\textsubscript{4} is up to 45 decreases over time, while hydrogen evolution increases (overall current increases)
- Reproduction runs showed reproducible values
- Nearly no CO und CH\textsubscript{4} products were found
- Stability over time
- Identification of the “real” catalyst?
- Stabilization of the “real” catalyst?
- Electrode formation?
- Electrode morphology?
- Transfer of catalyst to GDE possible
Summary CO₂-Electrolysis

CO₂ – Reduction to CO

• Current densities and system efficiencies can be raised by increasing electrolyte conductivities

• Increase of CO₂ gas flow allows a reduction to CO at higher current densities

• Increase of electrolyte flow increases achievable current densities

• Product gas separation has to be improved

• Gas-Diffusion-Electrodes with lower overpotential for CO and higher overpotential for H₂ will improve selectivity

CO₂ – Reduction to C₂H₄

• Faraday efficiencies of ~ 40% were achieved for the C₂H₄ formation at solid, but nano-functionalized copper electrodes

• Copper alloys (Sn, Zn, Al and their mixture) show also C₂H₄ formation.

• Stability of Electrodes under investigation

• Transfer of catalyst to Gas-Diffusion-Electrode started / Switching to flow cells in progress
(Earth-) Alkali Metal Combustion
Potential implementation matrix

**Charged energy carrier (seasonal)**

**Option 1**
- **Lithium**
- **combustion**
  - \( \text{CO}_2 \)
  - \( \text{CO} \)
  - \( \text{H}_2 \)
- **gasoline**
- **Conversion of \( \text{Li}_2\text{CO}_3 \) to \( \text{LiCl} \)**
- **LiCl Electrolysis**
- **recycling**

**Option 2**
- **combustion**
  - \( \text{N}_2 \) (air)
  - \( \text{Li}_3\text{N} \)
- **ammonia**
- **H\(_2\)O**
- **CO\(_2\) Absorber**
- **H\(_2\)O**

**Discharged energy carrier**
- \( \text{Li}_2\text{CO}_3 \)
Project Results
Spray Combustion and Flame Analysis

30 kW Lithium Reactor

- Ignition:
  - $T_{\text{Gas}}>T_{\text{Ignition}}$, HV-spark

- Stable, self-sustaining flame demonstrated
  - In air and CO$_2$

- Flame Temperature: ca. 2000 K

- Combustion products in CO$_2$:
  - Li$_2$CO$_3$, CO
Power to Value

**Compound based Energy Storage**

Overcapacity of Renewable Electricity

Energy + CO\textsubscript{2}

- Electro-catalysis

CO\textsubscript{2} from fossil-fired power plants

N\textsubscript{2} from air or IGCC or Oxyfuel plants

Via Li/Na/Mg... mediator

Synthetic fuels or chemical feedstock

**CO\textsubscript{2} To Value**

- Methane (CH\textsubscript{4})
  - Market Price: 81 €/t
  - Market Volume: > 2400 Mt/y

- Ethylene (C\textsubscript{2}H\textsubscript{4})
  - Market Price: 1000 €/t
  - Market Volume: 141 Mt/y

- Formic acid (HCOOH)
  - Market Price: 650 €/t (H\textsubscript{2} \rightarrow Naphtha)
  - Market Volume: 0.7 Mt/y

- Carbon monoxide (CO)
  - Market Price: 650 €/t (H\textsubscript{2} \rightarrow Naphtha)
  - Market Volume: > 210 000 Mt/y

**Li-Coal**

- Ammonia (NH\textsubscript{3})
  - Market Price: 500 €/t
  - Market Volume: 131 Mt/y