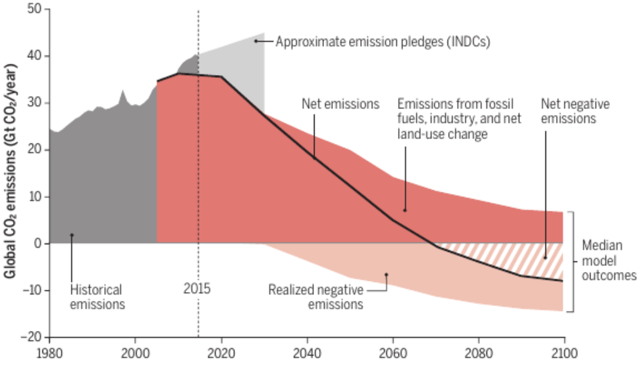
Photoelectrochemical CO_2 reduction as a negative emission technology

Matthias M. May[1], Kira Rehfeld[2]

1: Helmholtz-Zentrum Berlin, Institute for Solar Fuels. 2: Universität Heidelberg, Institute of Environmental Physics

DPG Spring Meeting Rostock
13.03.2019

Negative emissions



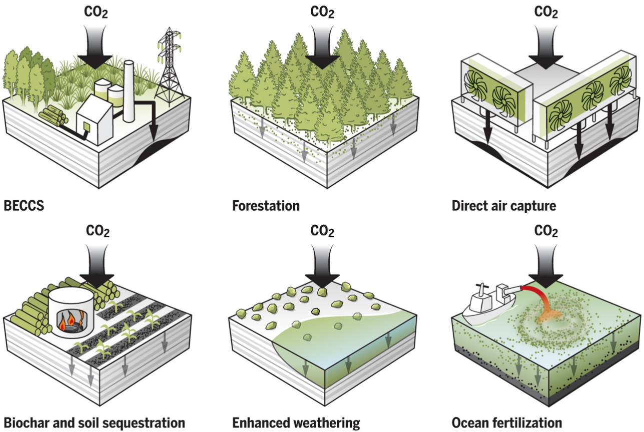
- Anthropogenic emission rates are reduced too slowly

→ Almost all climate models assume negative emissions, where energy is invested to sequester atmospheric CO_2, starting from 2030

- Type of technology and costs still very speculative

[1] Anderson and Peters, *Science* **354** (2016). [2] Hansen et al., *Earth Syst. Dyn.* **8** (2017).

Technologies



- Most considered technologies are based on natural photosynthesis
- Sequestration of CO_2 itself relies on (safe) mineral trapping [2]

[1] J. Rosen, *Science* **359** (2018). [2] Smith et al., *Nat. Clim. Change* **6** (2016).

Natural Photosynthesis

- Scalable!
- Long-term storage feasible
- *Energetic* efficiency ca. 2-3% [1]

→ **Large areas:**

- 10 Mio. km^2 for dedicated crops

[1] A. Melis, *Energy Environ. Sci.* **5** (2012). [2] Smith et al., *Nat. Clim. Change* **6** (2016).
[3] Heck et al., *Nat. Clim. Change* **8** (2018).

Natural Photosynthesis

- Scalable!
- Long-term storage feasible
- *Energetic* efficiency ca. 2-3% [1]

→ **Large areas:**

- 10 Mio. km^2 for dedicated crops

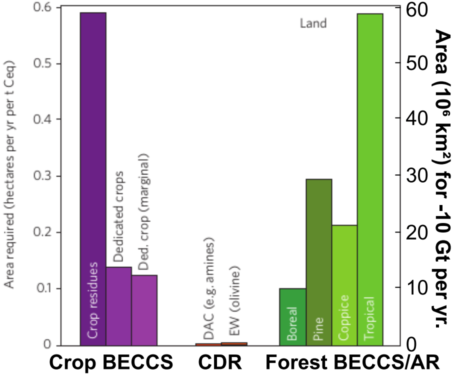
[1] A. Melis, *Energy Environ. Sci.* **5** (2012). [2] Smith et al., *Nat. Clim. Change* **6** (2016).
[3] Heck et al., *Nat. Clim. Change* **8** (2018).

Natural Photosynthesis

- Scalable!
- Long-term storage feasible
- *Energetic* efficiency ca. 2-3% [1]

→ **Large areas:**

- 10 Mio. km^2 for dedicated crops

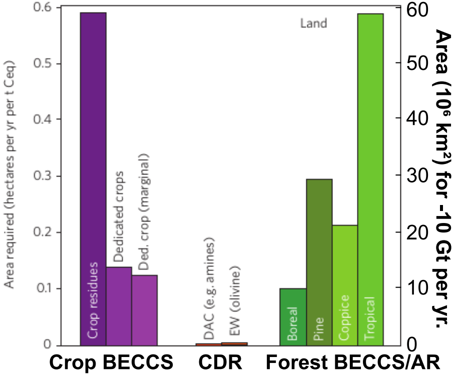


[1] A. Melis, *Energy Environ. Sci.* **5** (2012). [2] Smith et al., *Nat. Clim. Change* **6** (2016).
[3] Heck et al., *Nat. Clim. Change* **8** (2018).

- Scalable!
- Long-term storage feasible
- *Energetic* efficiency ca. 2-3% [1]

→ **Large areas:**

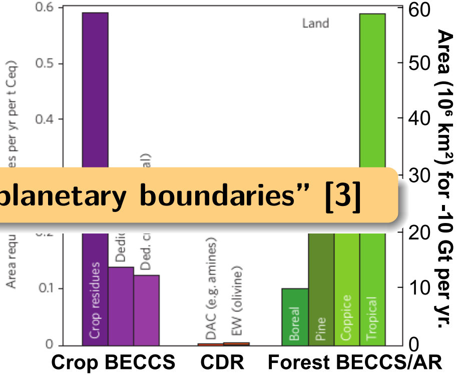
- 10 Mio. km^2 for dedicated crops



[1] A. Melis, *Energy Environ. Sci.* **5** (2012). [2] Smith et al., *Nat. Clim. Change* **6** (2016).
[3] Heck et al., *Nat. Clim. Change* **8** (2018).

Natural Photosynthesis

- Scalable!
- Long-term storage feasible
- *Energetic* efficiency ca. 2-3% [1]
- 10 Mio. km^2 for dedicated crops



"Difficult to reconcile with planetary boundaries" [3]

[1] A. Melis, *Energy Environ. Sci.* **5** (2012). [2] Smith et al., *Nat. Clim. Change* **6** (2016).
[3] Heck et al., *Nat. Clim. Change* **8** (2018).

Artificial Photosynthesis

- (Photo)electrochemical CO_2 reduction
- PV-coupled to dark electrolysis **or**
- Integrated systems

→ Challenges of PV & electrocatalysis

- For hydrogen, with 19% STH about 10x more efficient than its natural counterpart [1]

[1] Cheng, Richter, **May** et al., *ACS Energy Lett.* **3** (2018).

Artificial Photosynthesis

- (Photo)electrochemical CO_2 reduction
- PV-coupled to dark electrolysis **or**
- Integrated systems

→ Challenges of PV & electrocatalysis

- For hydrogen, with 19% STH about 10x more efficient than its natural counterpart [1]

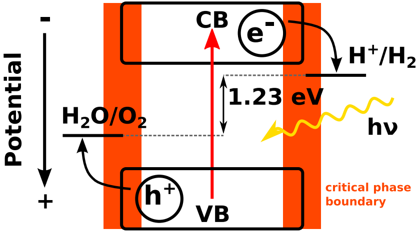
[1] Cheng, Richter, **May** et al., *ACS Energy Lett.* **3** (2018).

Artificial Photosynthesis

- (Photo)electrochemical CO_2 reduction
- PV-coupled to dark electrolysis **or**
- Integrated systems

→ Challenges of PV & electrocatalysis

- For hydrogen, with 19% STH about 10x more efficient than its natural counterpart [1]

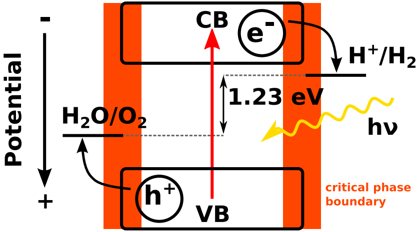


[1] Cheng, Richter, **May** et al., *ACS Energy Lett.* **3** (2018).

- (Photo)electrochemical CO_2 reduction
- PV-coupled to dark electrolysis **or**
- Integrated systems

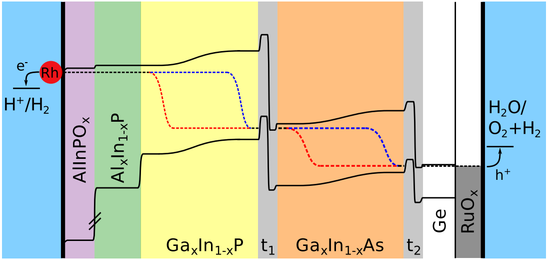
→ Challenges of PV & electrocatalysis

- For hydrogen, with 19% STH about 10x more efficient than its natural counterpart [1]



[1] Cheng, Richter, **May** et al., *ACS Energy Lett.* **3** (2018).

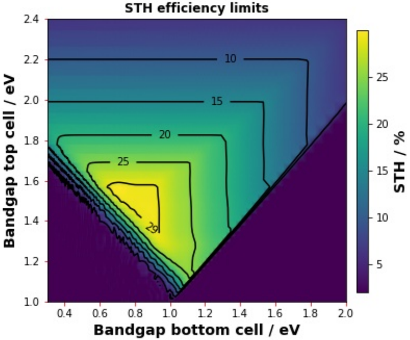
High efficiency



- Multi-junction absorbers required to produce $> 1.6\,\mathrm{V}$ photovoltage
- Suitable bandgap combinations, efficient catalysis
- Model using detailed balance, $\eta(j)$ from catalysis [2]
- For CO_2 reduction, STF efficiencies are a function of ΔG

[1] May et al., *Nat. Comm.* **6** (2015). [2] May, et al., Chapter 12 in *Integrated Solar Fuel Generators*, RSC (2018).

High efficiency



- Multi-junction absorbers required to produce $> 1.6\,\mathrm{V}$ photovoltage
- Suitable bandgap combinations, efficient catalysis
- Model using detailed balance, $\eta(j)$ from catalysis [2]
- For CO_2 reduction, STF efficiencies are a function of ΔG

[1] May et al., *Nat. Comm.* **6** (2015). [2] May, et al., Chapter 12 in *Integrated Solar Fuel Generators*, RSC (2018).

Solar-to-Carbon efficiency

- Solar-to-Fuel efficiencies:

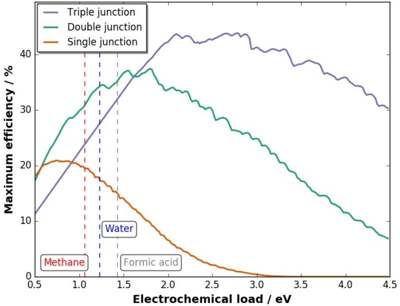
  $STF = \frac{\eta_F j_e \Delta G}{P \times e}$

→ Not suitable for neg. emissions

- Solar-to-carbon (STC) [2]:

  $STC = \frac{\eta_F \eta_e j_e}{j_{ph}}$

- Large impact of η_e on STC



[1] May, et al., Chapter 12 in *Integrated Solar Fuel Generators*, RSC (2018). [2] May and Rehfeld, *Earth Syst. Dyn.* **10** (2019).

Solar-to-Carbon efficiency

- Solar-to-Fuel efficiencies:

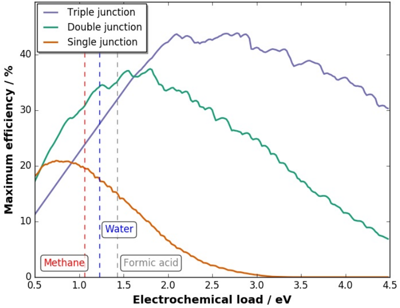
  $\mathrm{STF} = \frac{\eta_F j_e \Delta G}{P \times e}$

$\rightarrow$ Not suitable for neg. emissions

- Solar-to-carbon (STC) [2]:

  $\mathrm{STC} = \frac{\eta_F \eta_e j_e}{j_{ph}}$

- Large impact of η_e on STC



[1] May, et al., Chapter 12 in *Integrated Solar Fuel Generators*, RSC (2018). [2] May and Rehfeld, *Earth Syst. Dyn.* **10** (2019).

Solar-to-Carbon efficiency

- Solar-to-Fuel efficiencies:

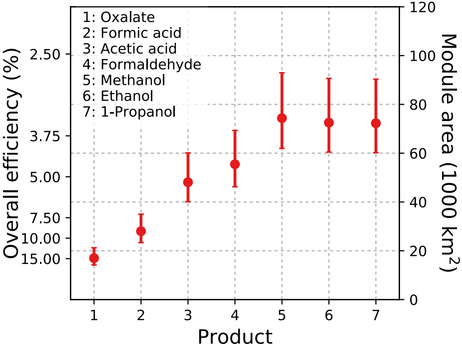
  $$STF = \frac{\eta_F j_e \Delta G}{P \times e}$$

→ Not suitable for neg. emissions

- Solar-to-carbon (STC) [2]:

  $$\mathrm{STC} = \frac{\eta_F \eta_e j_e}{j_{ph}}$$

- Large impact of η_e on STC



[1] May, et al., Chapter 12 in *Integrated Solar Fuel Generators*, RSC (2018). [2] May and Rehfeld, *Earth Syst. Dyn.* **10** (2019).

Solar-to-Carbon efficiency

- Solar-to-Fuel efficiencies:

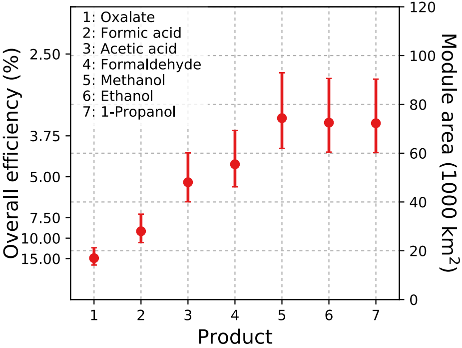
  $\text{STF} = \frac{\eta_F j_e \Delta G}{P \times e}$

$\rightarrow$ Not suitable for neg. emissions

- Solar-to-carbon (STC) [2]:

  $\text{STC} = \frac{\eta_F \eta_e j_e}{j_{ph}}$

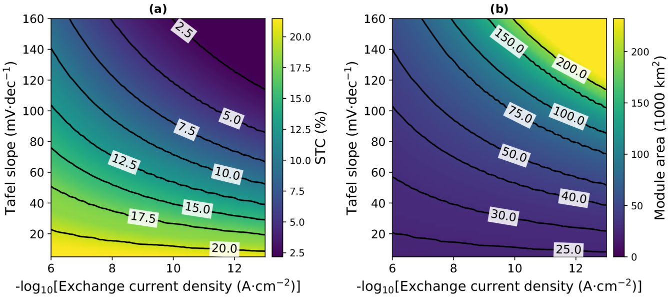
- Large impact of η_e on STC



e per carbon: 1 for oxalate; 2 for formic acid; 4 for acetic acid & formaldehyde; 6 for methanol, ethanol, 1-propanol

[1] May, et al., Chapter 12 in *Integrated Solar Fuel Generators*, RSC (2018). [2] May and Rehfeld, *Earth Syst. Dyn.* **10** (2019).

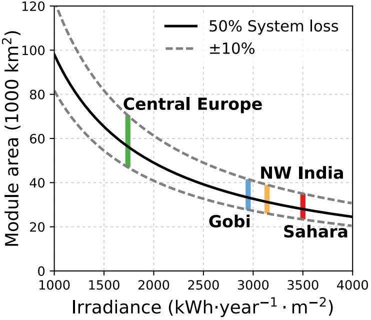
Required area



- Catalyst performance crucial
- Desert areas interesting due to high irradiance
- Water consumption (formic acid): ca. 5 km^3 as opposed to $>$ 2000 km^3 for biomass [2]

[1] May and Rehfeld, *Earth Syst. Dyn.* **10** (2019). [2] Heck et al., *Nat. Clim. Change* **8** (2018).

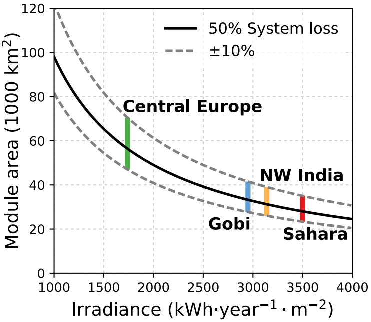
Required area



- Catalyst performance crucial
- Desert areas interesting due to high irradiance
- Water consumption (formic acid): ca. 5 km^3 as opposed to $>$ 2000 km^3 for biomass [2]

[1] May and Rehfeld, *Earth Syst. Dyn.* **10** (2019). [2] Heck et al., *Nat. Clim. Change* **8** (2018).

Required area



- Catalyst performance crucial
- Desert areas interesting due to high irradiance
- Water consumption (formic acid): ca. 5 km^3 as opposed to $> 2000\,km^3$ for biomass [2]

[1] May and Rehfeld, *Earth Syst. Dyn.* **10** (2019). [2] Heck et al., *Nat. Clim. Change* **8** (2018).

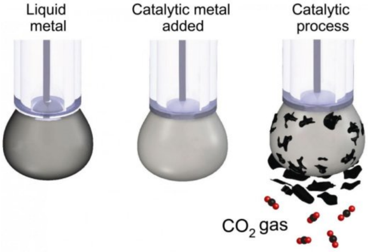
Challenges

- Storage
- Could be alleviated by chemical post-processing, e.g. oxalate to organic minerals [1]
- Electrochemical production of solid carbon also feasible [2]
- Catalysts

[1] B. Parkinson, *Earth Syst. Dynam. Discuss.* DOI:10.5194/esd-2018-53-RC1. [2] Esrafilzadeh et al. *Nat. Comm.* **10** (2019).

Challenges

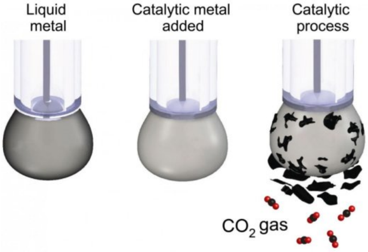
- Storage
- Could be alleviated by chemical post-processing, e.g. oxalate to organic minerals [1]
- Electrochemical production of solid carbon also feasible [2]
- Catalysts



[1] B. Parkinson, *Earth Syst. Dynam. Discuss.* DOI:10.5194/esd-2018-53-RC1. [2] Esrafilzadeh et al. *Nat. Comm.* **10** (2019).

Challenges

- Storage
- Could be alleviated by chemical post-processing, e.g. oxalate to organic minerals [1]
- Electrochemical production of solid carbon also feasible [2]
- Catalysts



[1] B. Parkinson, *Earth Syst. Dynam. Discuss.* DOI:10.5194/esd-2018-53-RC1. [2] Esrafilzadeh et al. *Nat. Comm.* **10** (2019).

Summary & Outlook

HZB Helmholtz Zentrum Berlin

- Current climate policies require large-scale CO_2 removal from 2030 on
- *Natural photosynthesis* offers ease of storage, but requires large areas
- *Artificial photosynthesis* reduces land and water footprint, but will probably be expensive → **Solar-To-Carbon** efficiency as benchmark
- **Avoiding** CO_2 emissions, e.g. by Solar Fuels, is always preferable

Summary & Outlook

HZB Helmholtz Zentrum Berlin

- Current climate policies require large-scale CO_2 removal from 2030 on
- *Natural photosynthesis* offers ease of storage, but requires large areas
- *Artificial photosynthesis* reduces land and water footprint, but will probably be expensive $\rightarrow$ **Solar-To-Carbon** efficiency as benchmark
- **Avoiding** CO_2 emissions, e.g. by Solar Fuels, is always preferable

Summary & Outlook

HZB Helmholtz Zentrum Berlin

- Current climate policies require large-scale CO_2 removal from 2030 on
- *Natural photosynthesis* offers ease of storage, but requires large areas
- *Artificial photosynthesis* reduces land and water footprint, but will probably be expensive → **Solar-To-Carbon** efficiency as benchmark
- **Avoiding** CO_2 emissions, e.g. by Solar Fuels, is always preferable

Thanks for your attention!

Financial support:

Leopoldina Nationale Akademie der Wissenschaften

unisyscat