# Oxygen Integration in $CO_2$-Electrochemical-Reduction-based Seasonal Storage System

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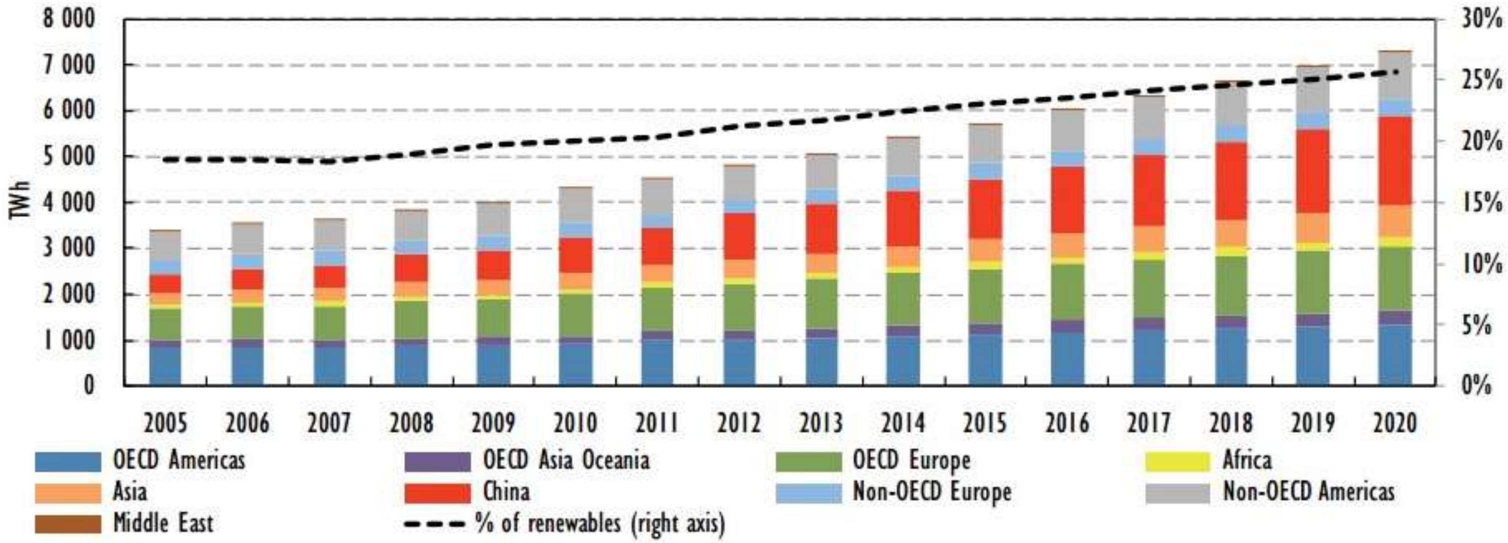
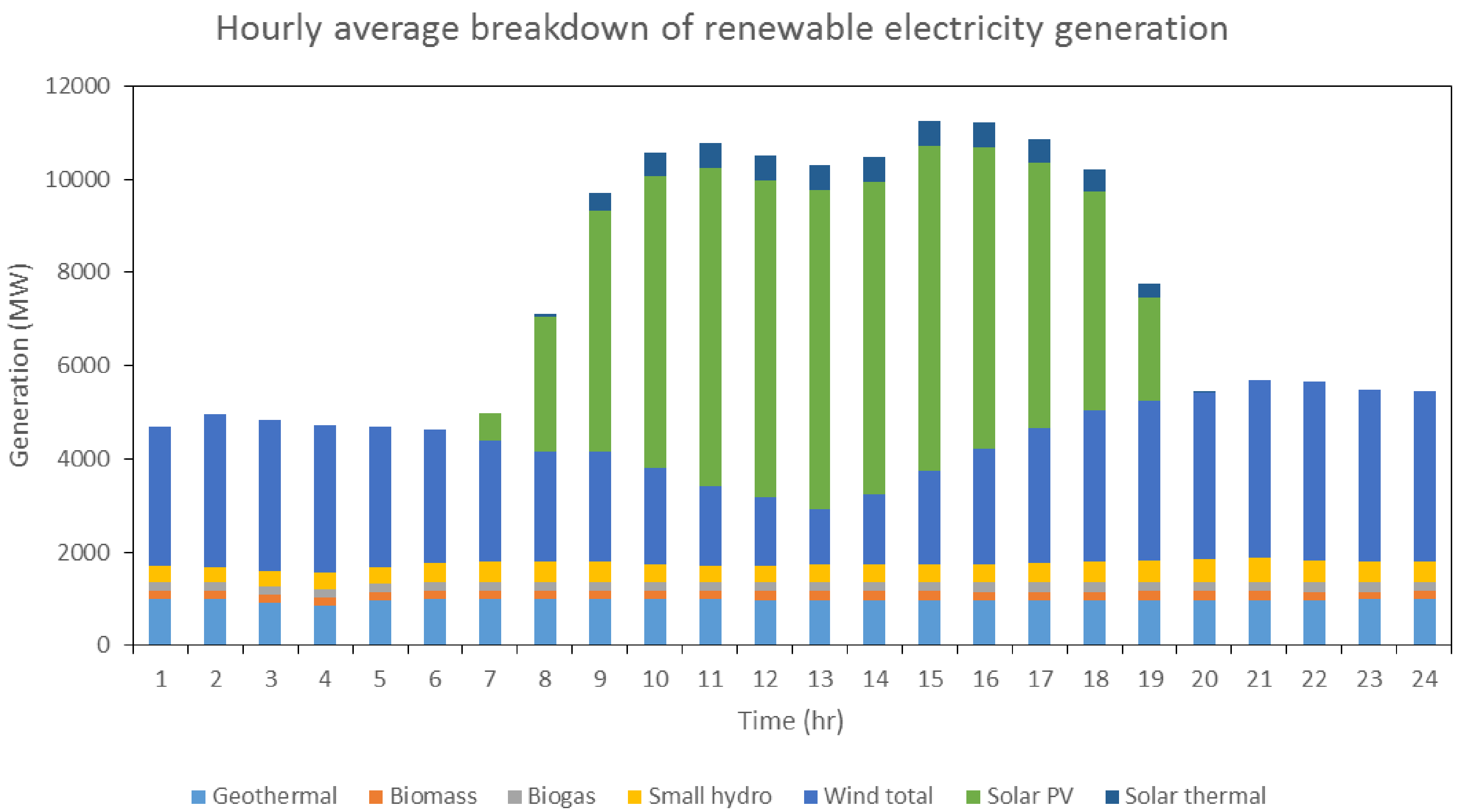
# Introduction: development of renewable energy



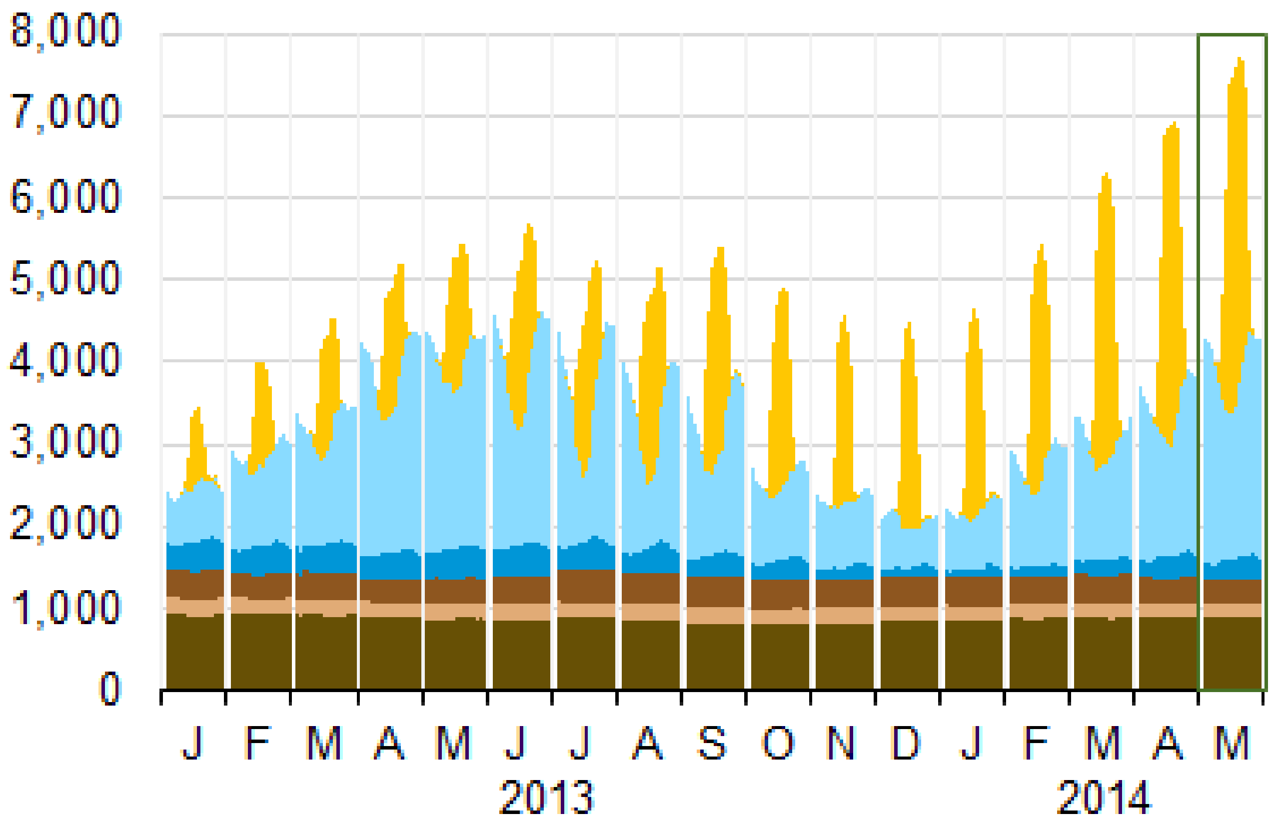

**Source:** IEA, Medium-Term Renewable Energy Market Report 2014: Market Analysis and Forecasts to 2020, 2014. http://www.iea.org/bookshop/708-Medium-Term_Renewable_Energy_Market_Report_2015

# Intermittency of renewable energy: diurnal



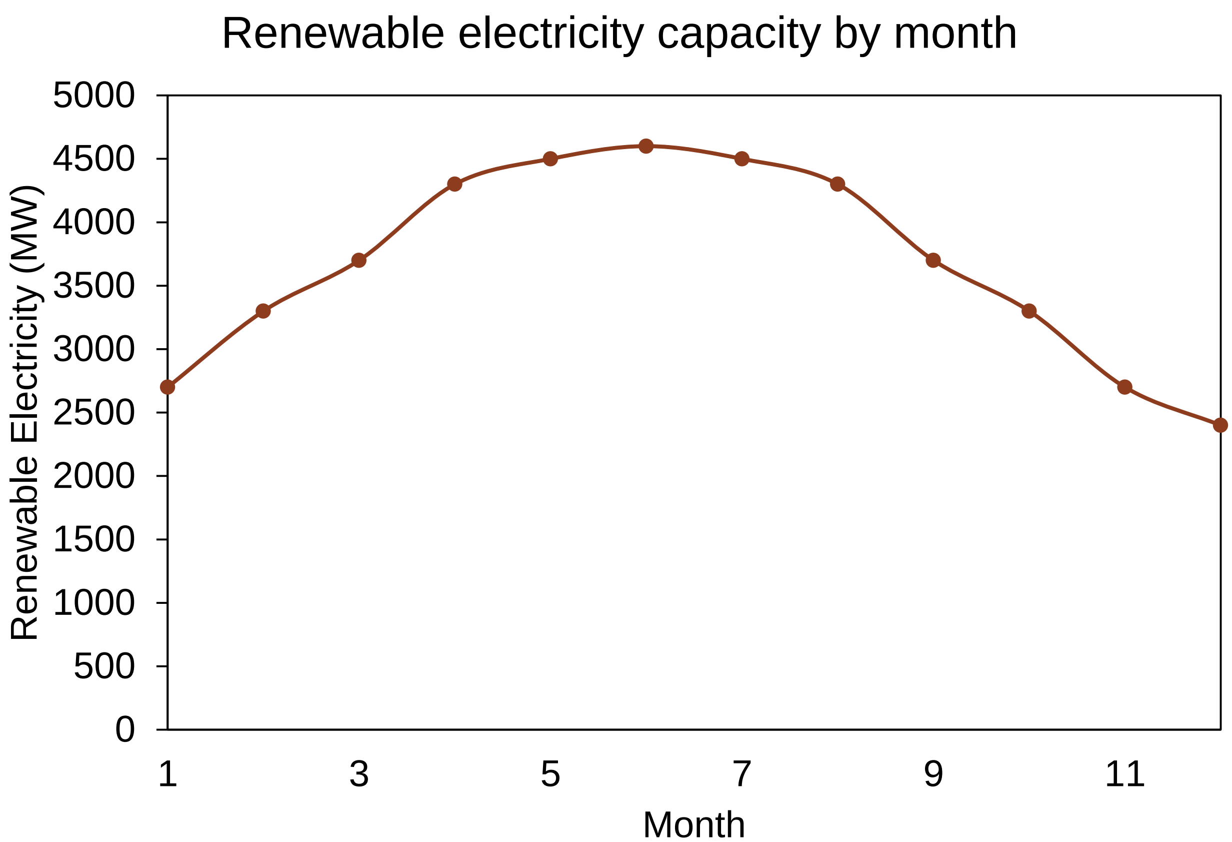

**Source:** CAISO Daily Renewables Watch, Date: 05. 10. 16.
http://content.caiso.com/green/renewrpt/20160509_DailyRenewablesWatch.txt

# Intermittency of renewable energy: seasonal




**Source:** EIA replotted from CAISO data; **Note:** This chart shows a set of 24 hours for each month, calculated from CAISO's average hourly output data by taking the average output for each hour in a given month. http://www.eia.gov/todayinenergy/detail.cfm?id=16851#tabs_SpotPriceSlider-2

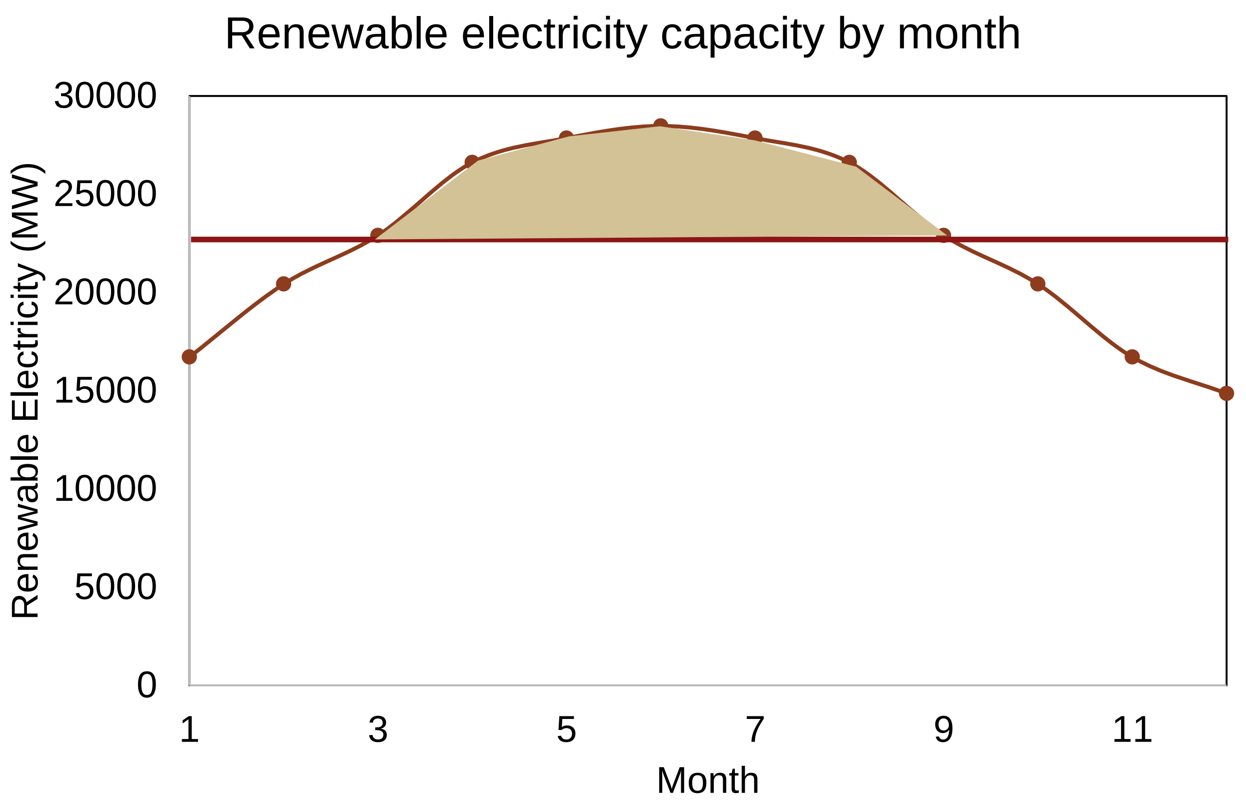
# Seasonal storage: large storage capacity needed




CA electricity generation in 2014 : ~ 200 TWh Generation

**Source:** EIA, California Electricity Profile 2014, http://www.eia.gov/electricity/state/california/index.cfm

# Seasonal storage: large storage capacity needed




Seasonal energy storage needed in CA: 17.5 TWh

# Seasonal storage: large storage capacity needed

For 17.5 TWh:

- Lithium ion batteries energy density: 200 Wh/kg or 400 Wh/L
- Stored in Li-ion batteries: $4.4 \times 10^7$ m$^3$

- If it is stored in Li-ion batteries: $8.8 \times 10^7$ ton; $2.63 \times 10^6$ ton Li.
- Roughly 1000 times of current lithium global production

**Source:** USGS, http://minerals.usgs.gov/minerals/pubs/commodity/lithium/

# Seasonal storage: large storage capacity needed

If lithium ion batteries are not an option for seasonal storage:

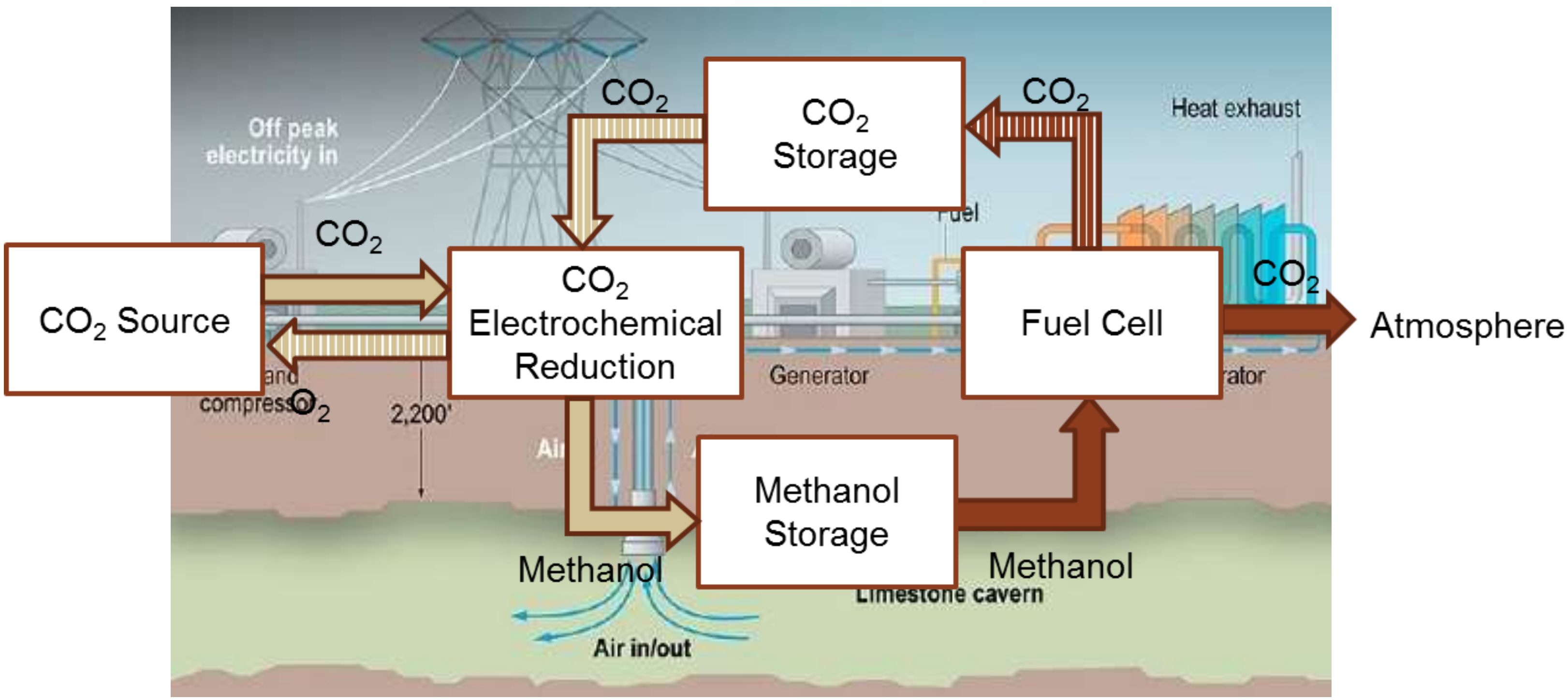



Image credit: Wikipedia, pumped hydro storage; NREL, compressed air energy storage; http://en.wikipedia.org/wiki/Pumped-storage_hydroelectricity; 2013/04/storing-renewable-energy-pumped-storage-compressed-air-molten-salt-hydrogen-more/

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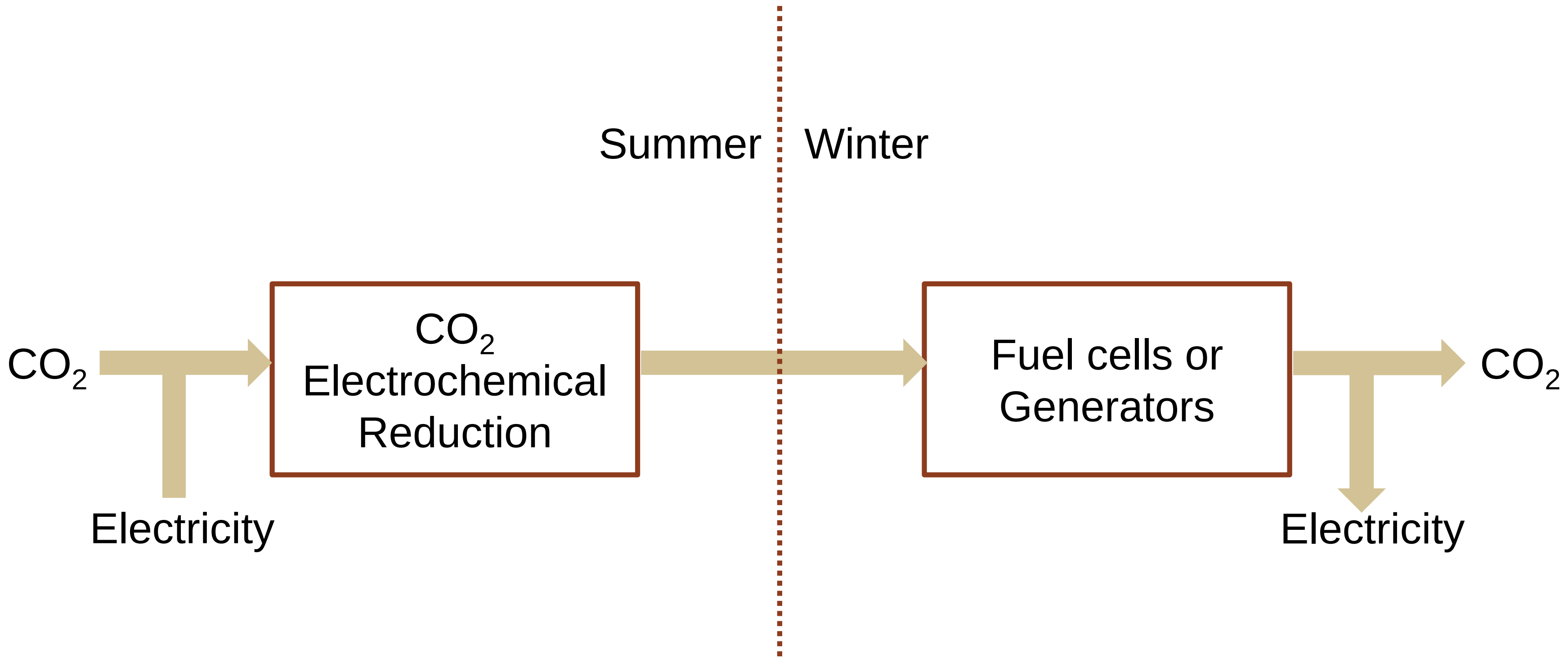
# Reduction of $CO_2$ for long-term storage




$CO_2 + H_2O \rightarrow \text{Fuel} + O_2$

$\text{Fuel} + O_2 \rightarrow CO_2 + H_2O$

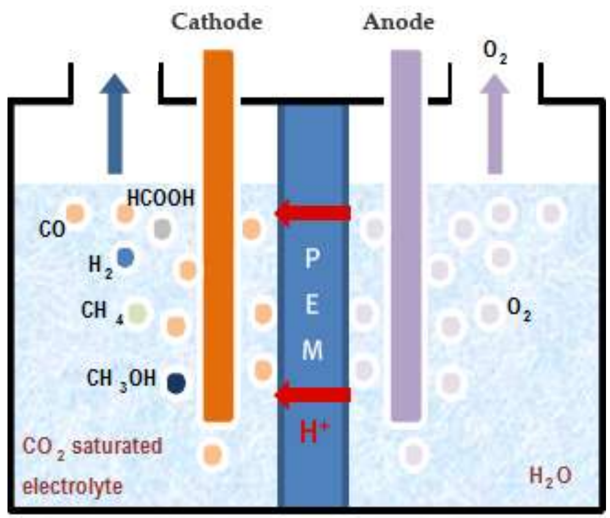
# An arcane art

Henri Julien Dumont, The alchemist, oil on Canvas

Chemists corner, cosmetic chemists, 2016

# What is electrochemical reduction of $CO_2$?

- Cathode: reduction
- $CO_2 + 6H^+ + 6e^- = CH_3OH + H_2O$
- $E^\theta$: 0.03V



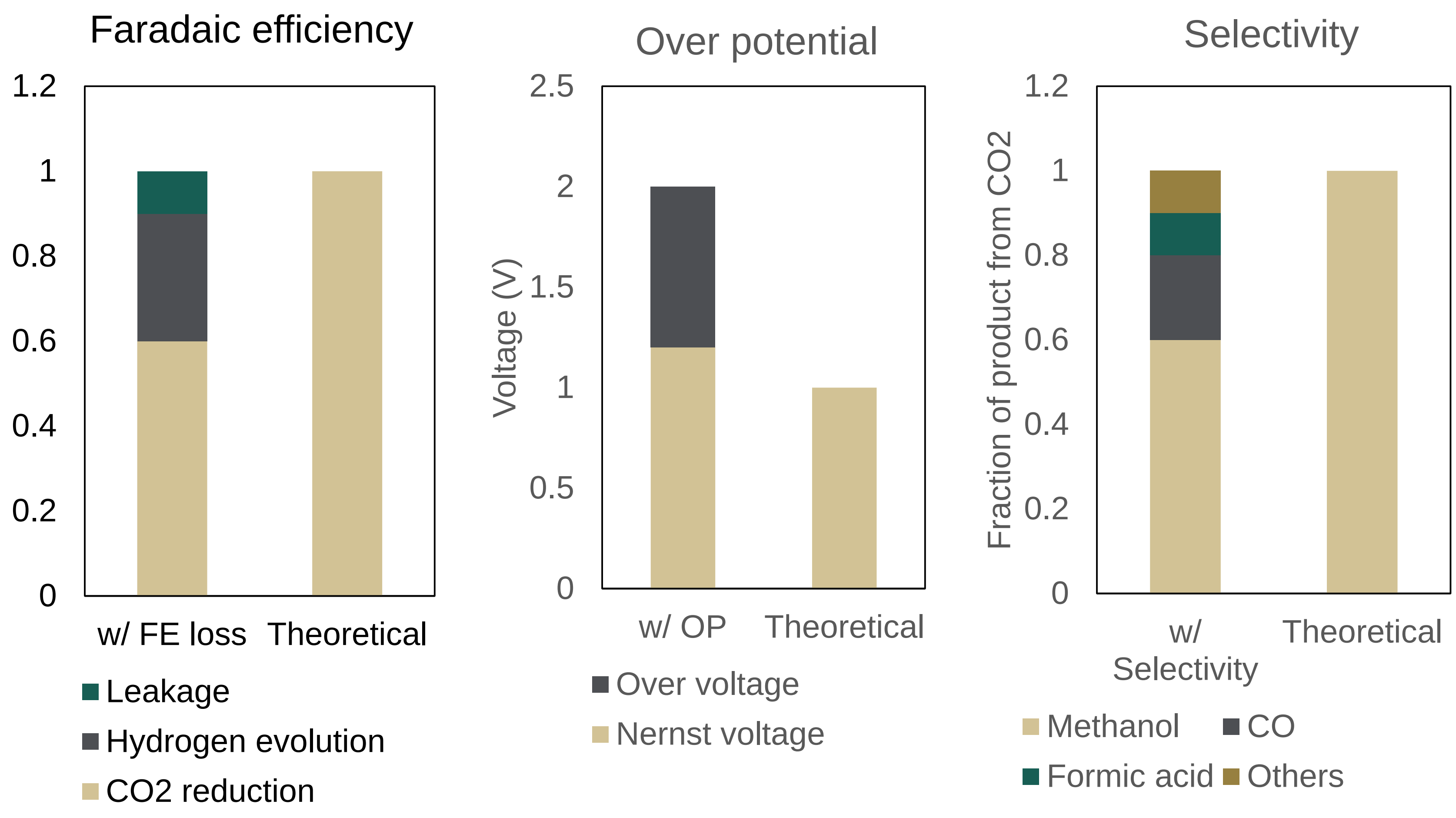
Electrochemical $CO_2$ Conversion System

- Anode: oxidation
- Anode: $3H_2O = 6H^+ + 3/2O_2 + 6e^-$
- $E^\theta$: 1.20V

- Takeaway
  - 1. requires large amount of energy
  - 2. transform $CO_2$ into an oxidizable form
  - 3. Produces oxygen

Image credit: Energy Nano Materials and Process lab of Chung-Ang University. https://enpl.cau.ac.kr/20150612/sub03/sub0303.php

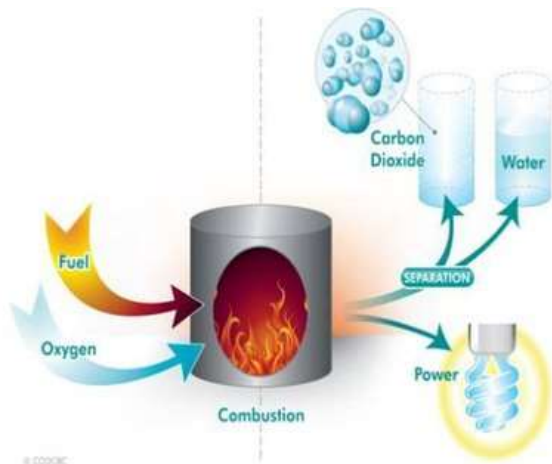
# Three key parameters of $CO_2$ electrolyzers





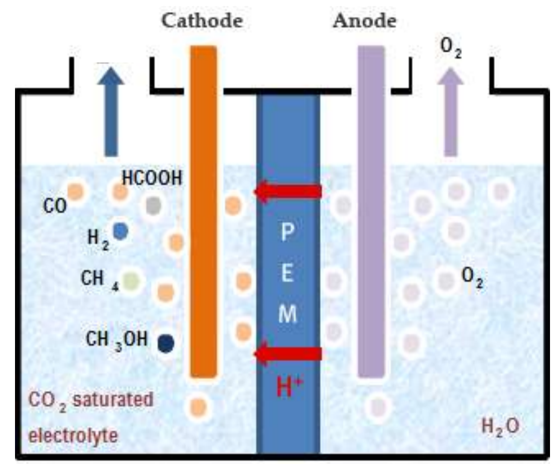
**Source:Studt, Felix, et al. "Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol." Nature chemistry 6.4 (2014): 320-324.**
Spataru, Nicolae, et al. "Electrochemical reduction of carbon dioxide at ruthenium dioxide deposited on boron-doped diamond." Journal of applied electrochemistry 33.12 (2003): 1205-1210.
Watanabe, Masahiro, et al. "Design of Alloy Electrocatalysts for CO 2 Reduction III. The Selective and Reversible Reduction of on Cu Alloy Electrodes." *Journal of the Electrochemical Society* 138.11 (1991): 3382-3389.
Minh Tuyen H, Le. *Electrochemical Reduction of CO2 to Methanol*. Diss. Louisiana State University and, 2011.
Qu, Jianping, et al. "Electrochemical reduction of CO 2 on RuO 2/TiO 2 nanotubes composite modified Pt electrode." *Electrochimica Acta* 50.16 (2005): 3576-3580.
Hori, Yoshio, et al. "Electrocatalytic process of CO selectivity in electrochemical reduction of CO 2 at metal electrodes in aqueous media." *Electrochimica Acta* 39.11 (1994): 1833-1839.
Ishimaru, S., R. Shiratsuchi, and G. Nogami. "Pulsed Electroreduction of CO 2 on Cu-Ag Alloy Electrodes." *Journal of The Electrochemical Society* 147.5 (2000): 1864-1867.
Kuhl, Kendra P., et al. "New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces." *Energy & Environmental Science* 5.5 (2012): 7050-7059.

# What to do with the $O_2$?




$CO_2$

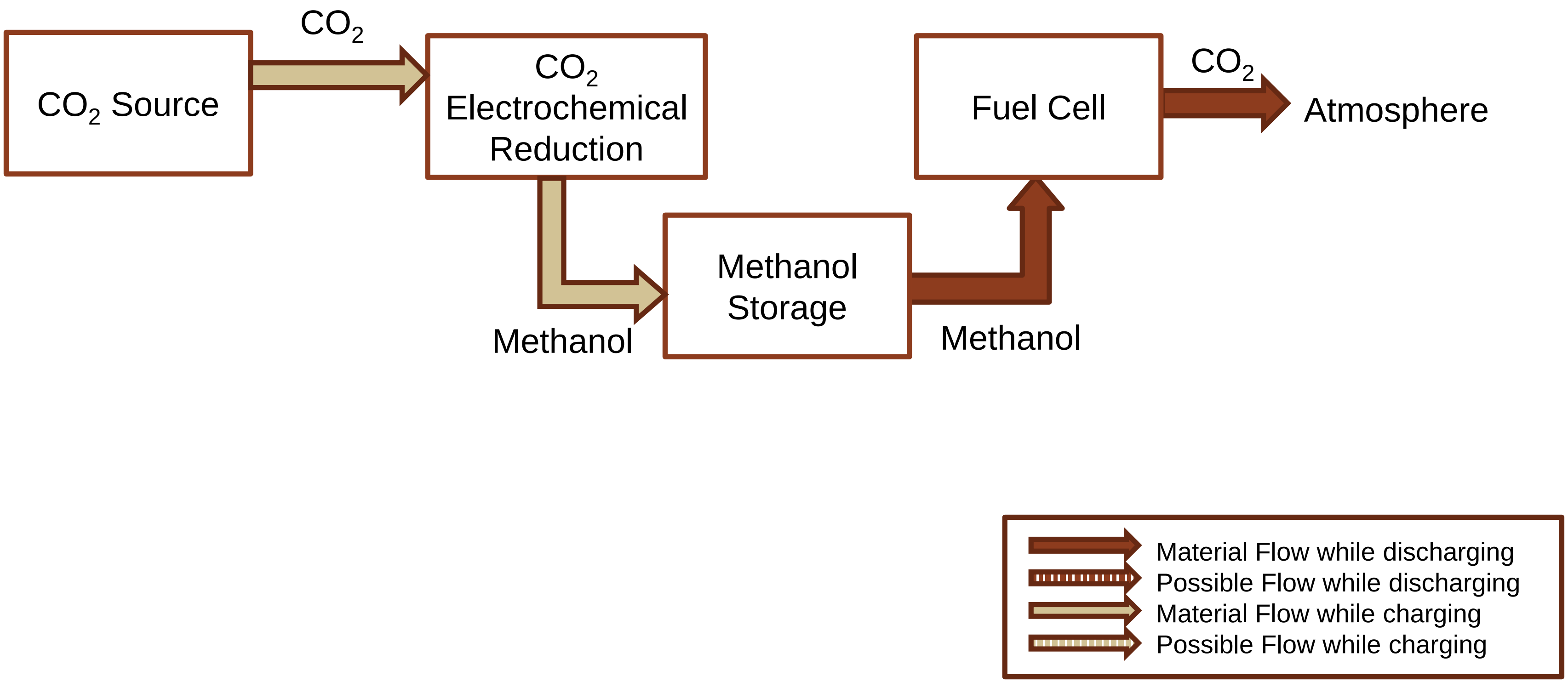
$O_2$



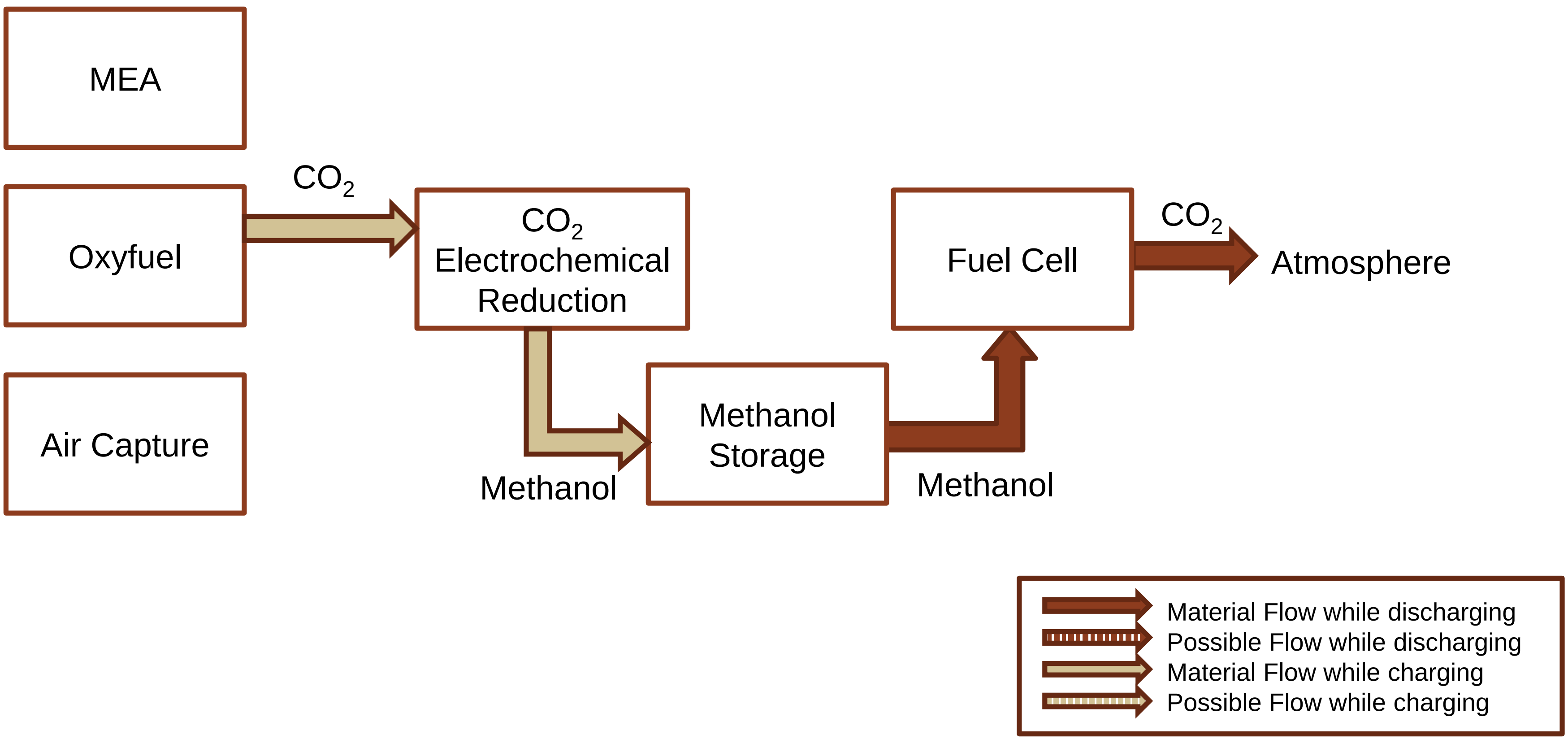

Electrochemical $CO_2$ Conversion System

Image credit: Oresome Resources, Oxycombustion process, http://www.oresomeresources.com/ media_centre_view/ resource/ image_oxyfiring_combustion/category/coal_low_emission/section/media/parent/
Energy Nano Materials and Process lab of Chung-Ang University. https://enpl.cau.ac.kr/20150612/sub03/sub0303.php

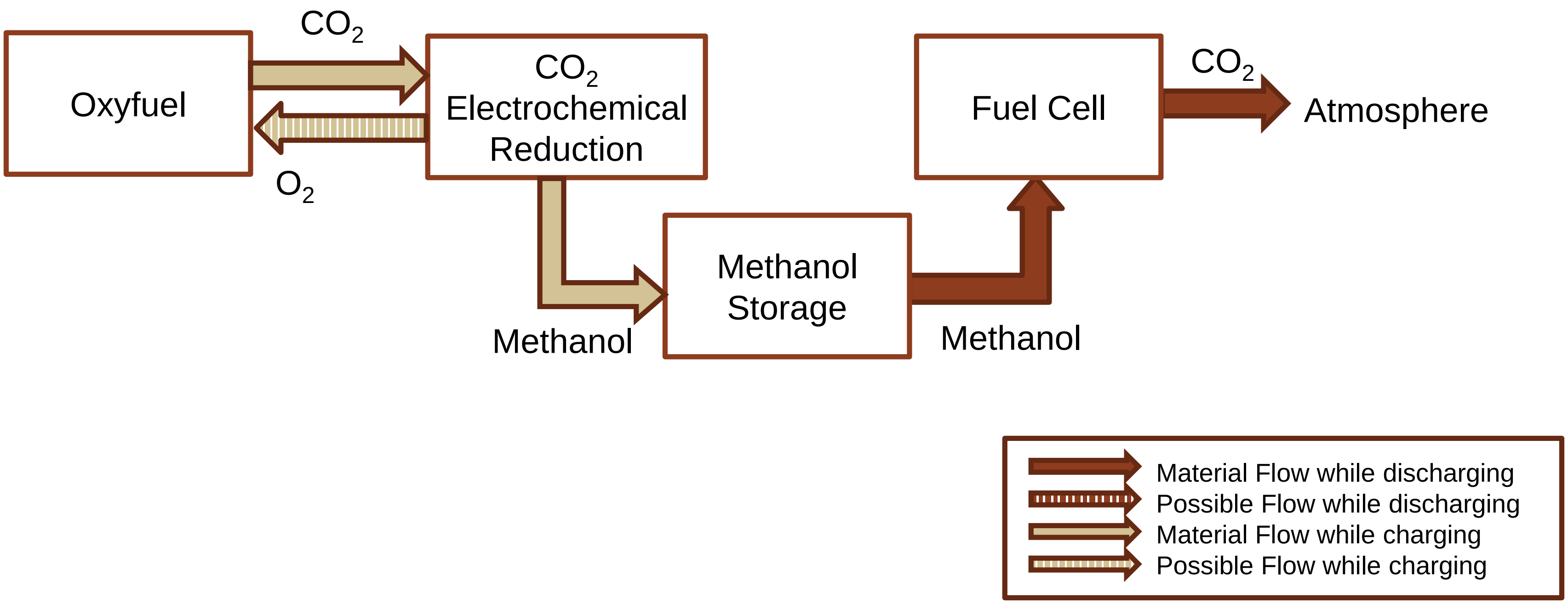
# Model: Seasonal storage system



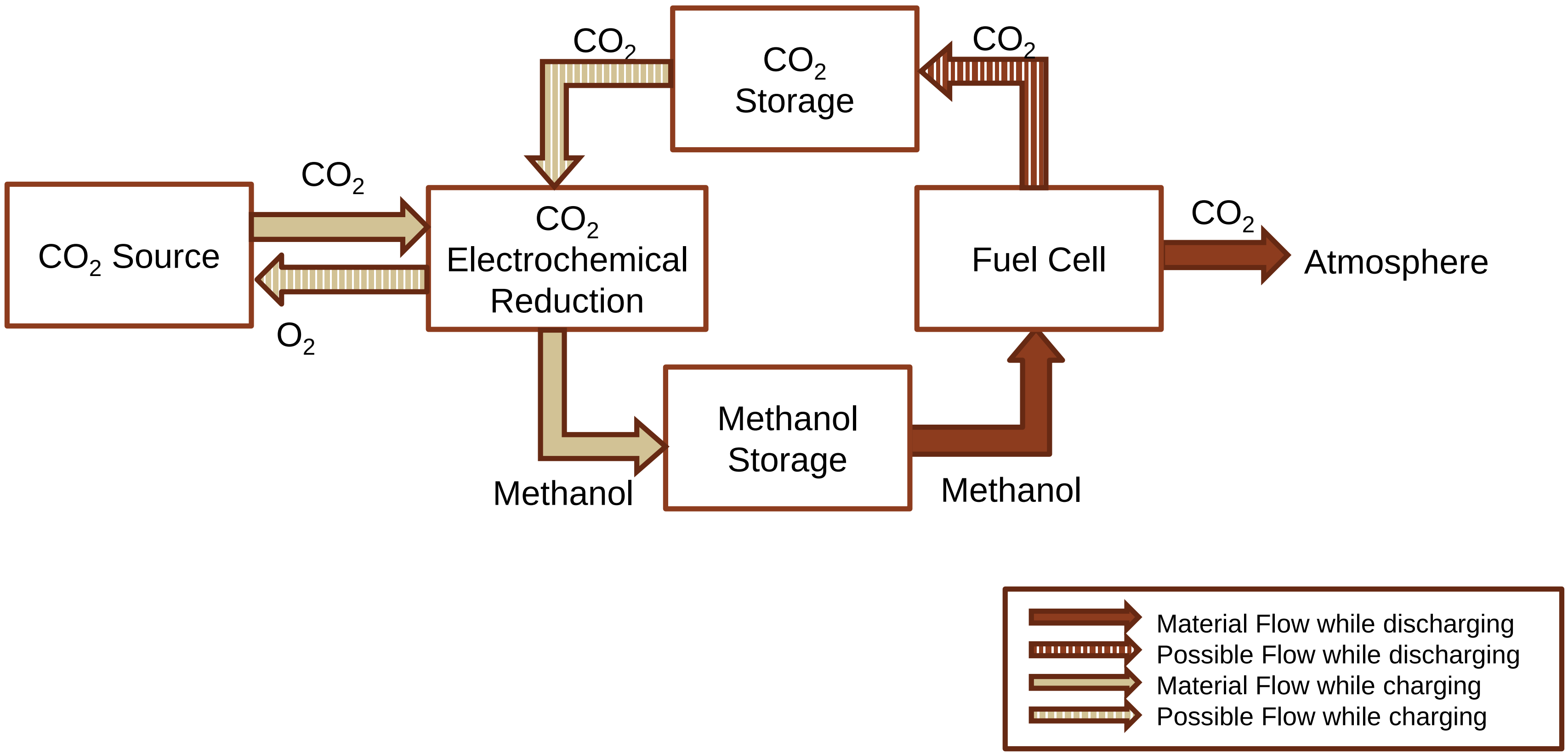
# Design Choice 1: $CO_2$ source



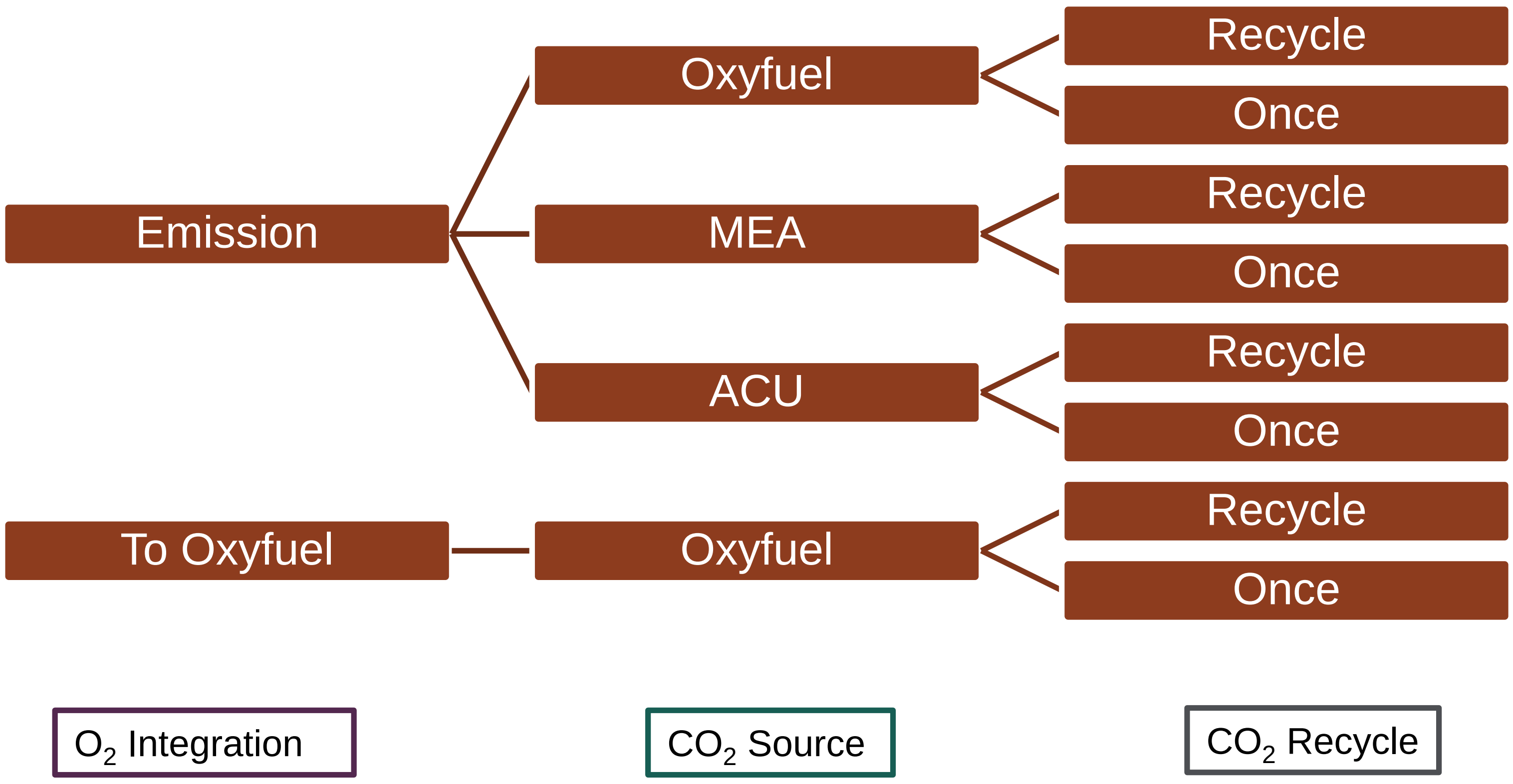
# Design Choice 2



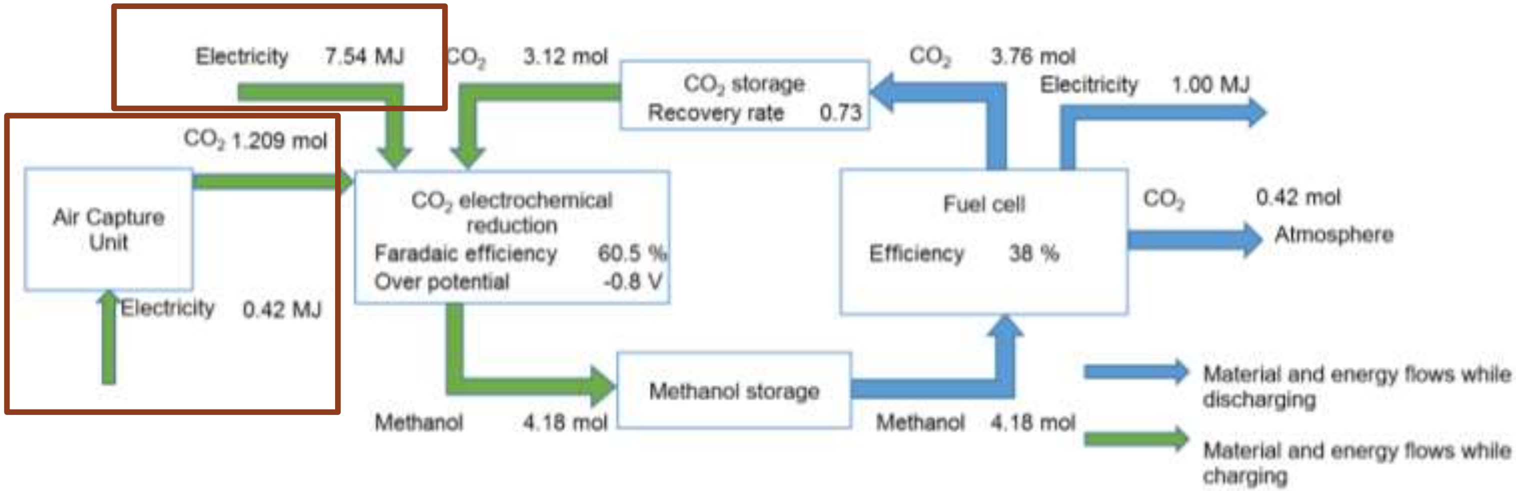
# Design Choice 3: $CO_2$ Recycling



# System Design



# 1. $CO_2$ Sources



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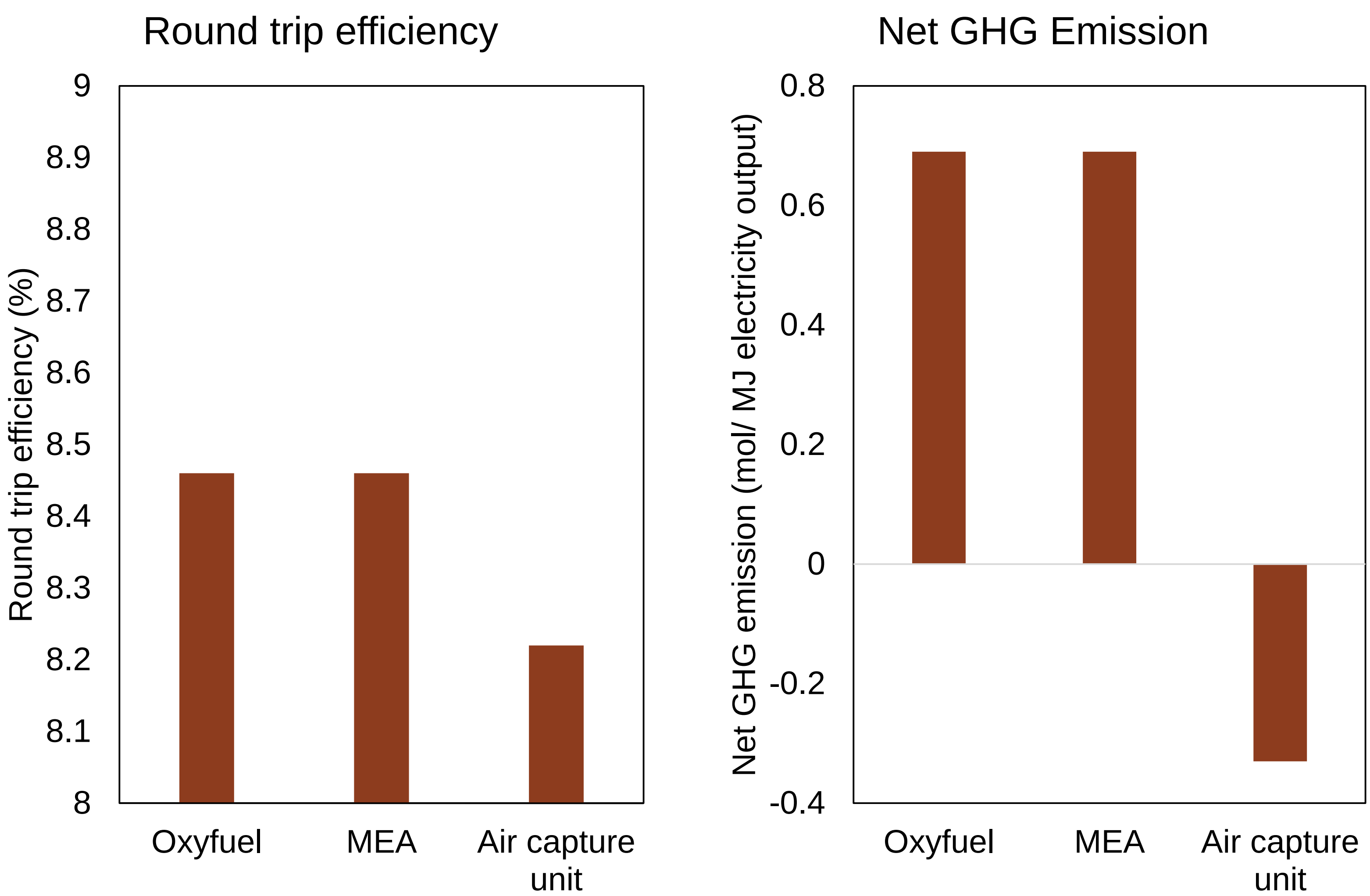
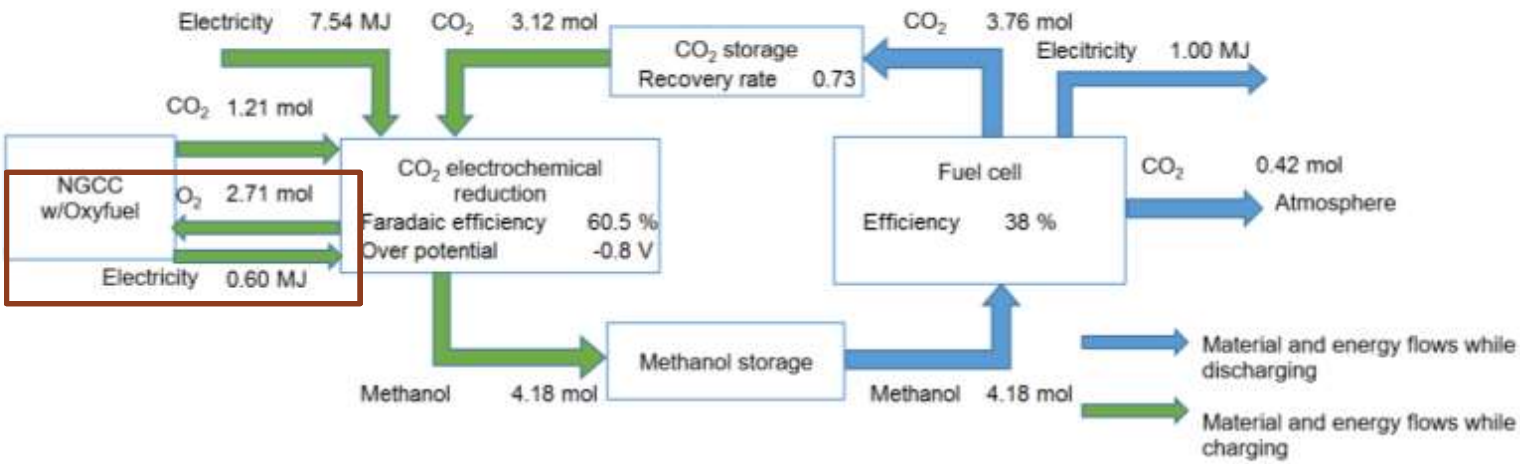
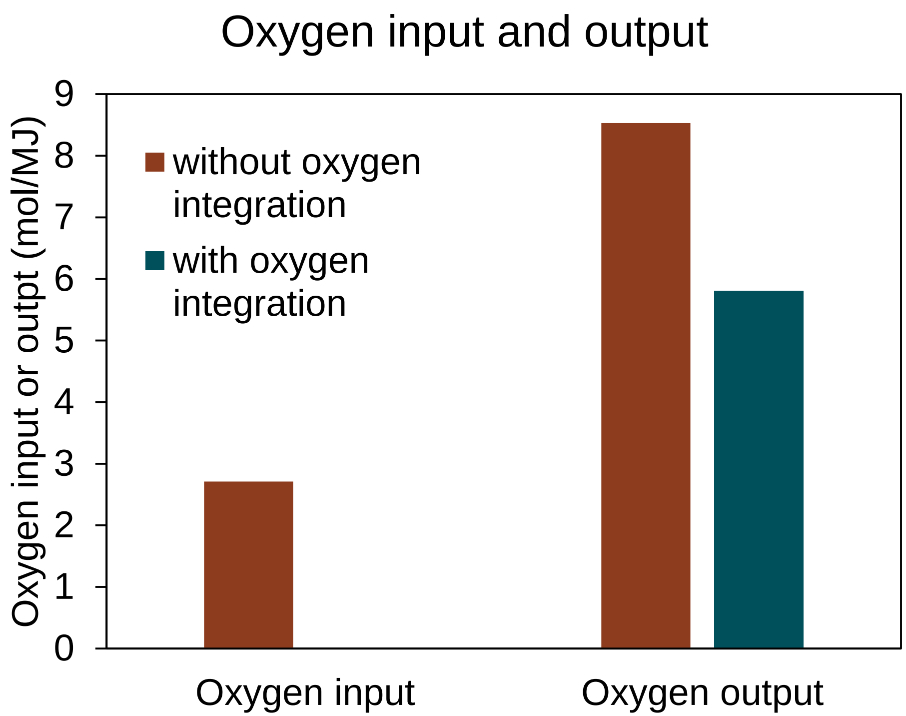
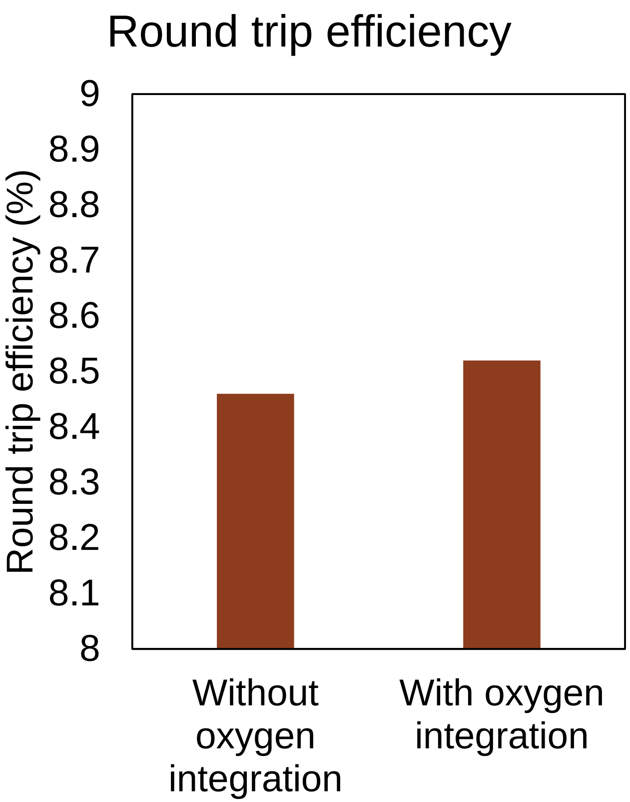


# 2. Oxygen Integration

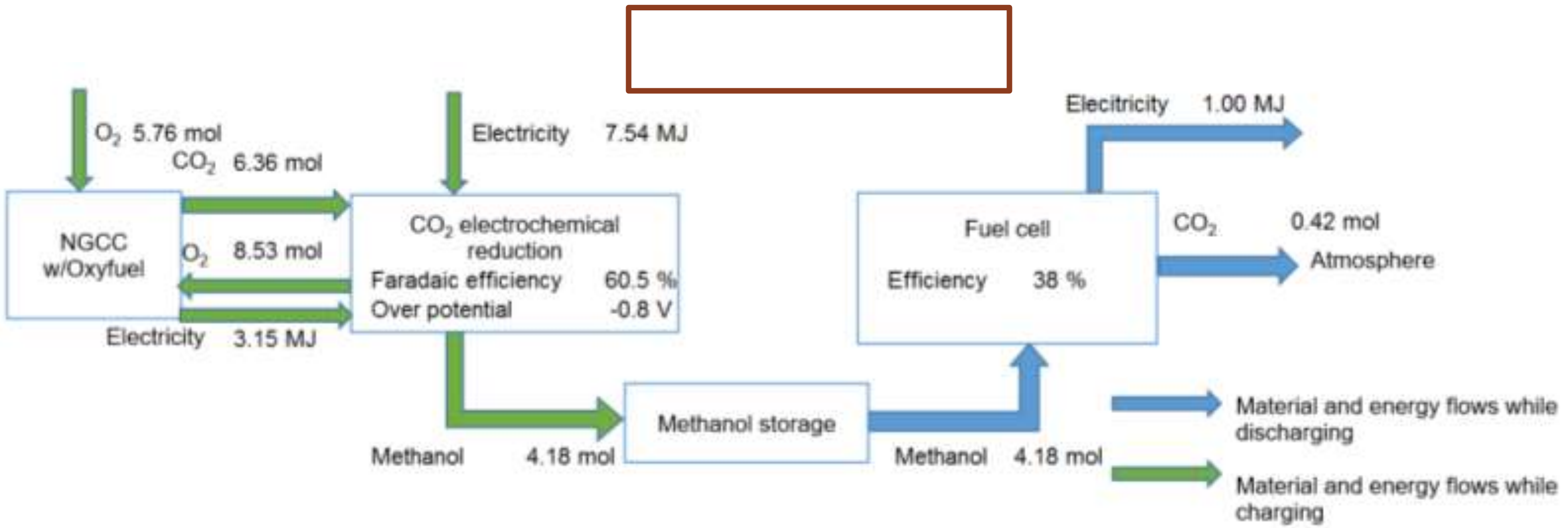


# 2. Oxygen Integration – Mass balance and performance



# 3. $CO_2$ Recycling



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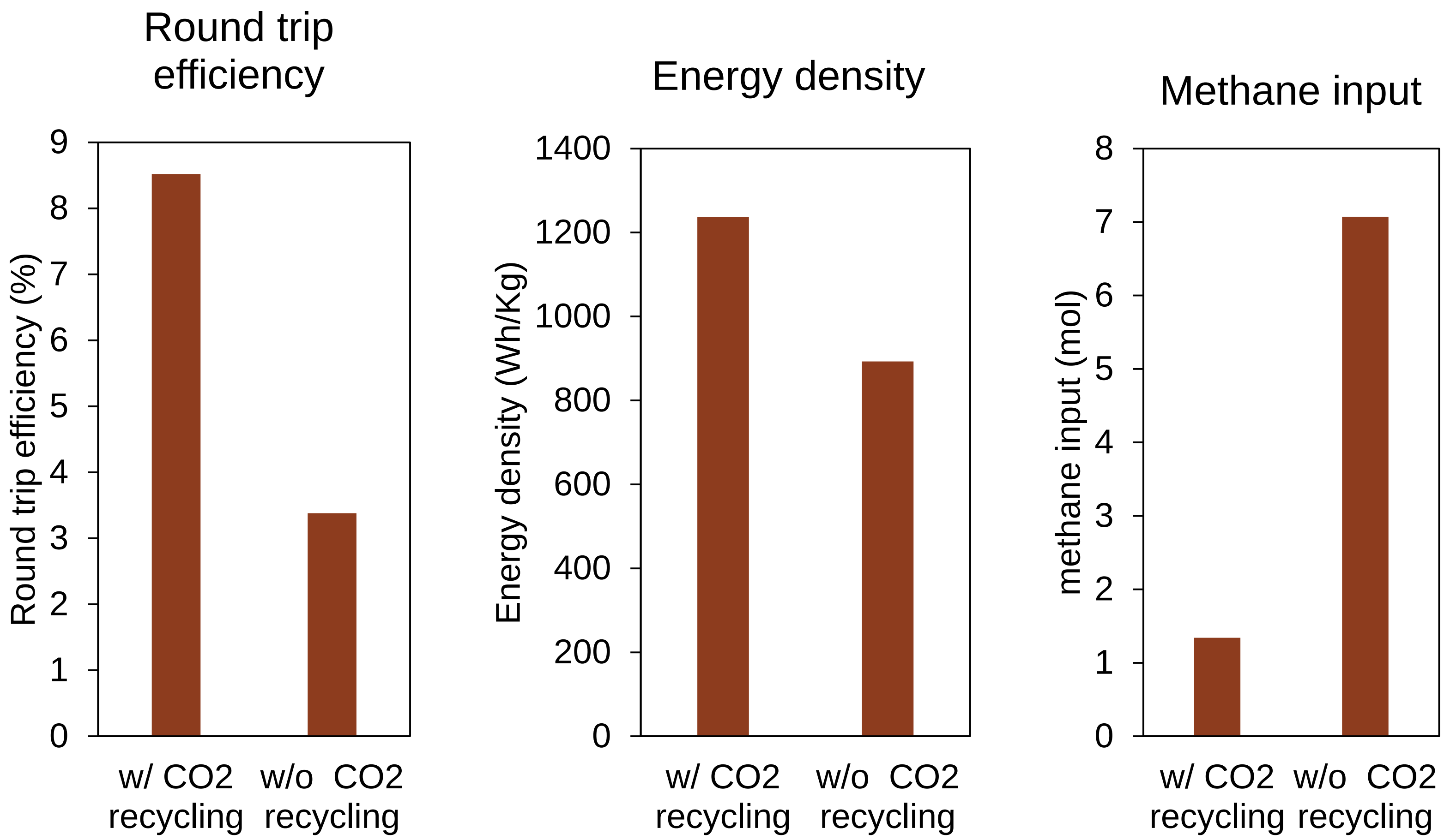
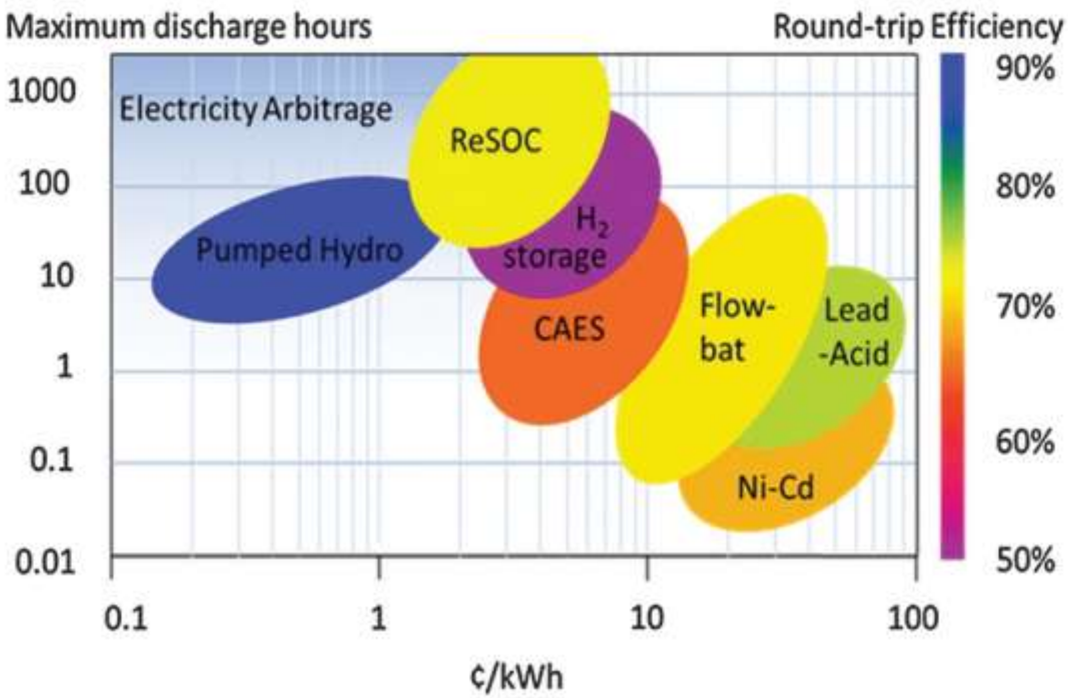


# Conclusions

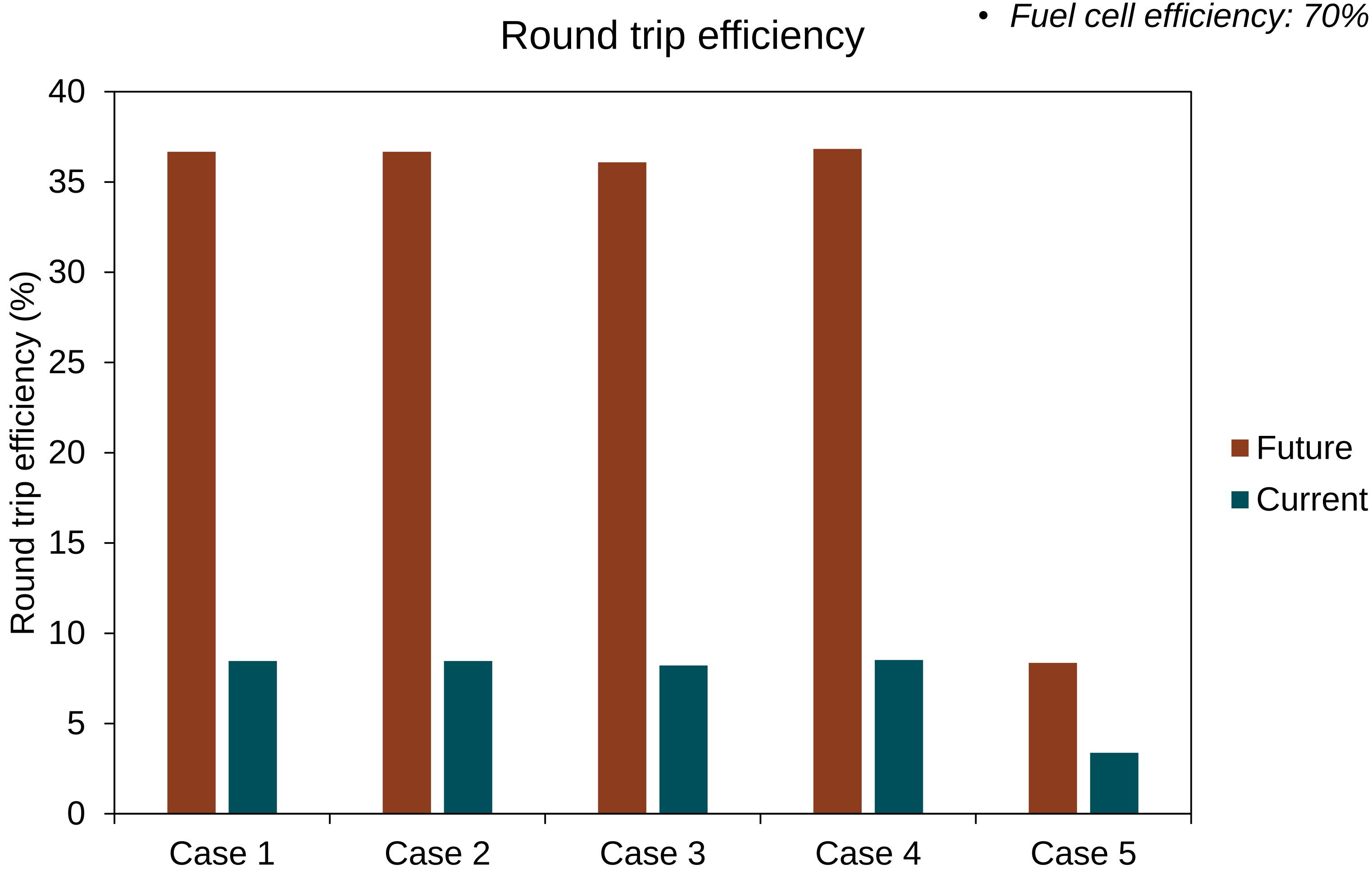
1. Does oxygen integration make sense?
   - Yes, but by a small margin
2. Does CO2 reduction as a battery makes sense?
   - Not really with current technology




Source: Jensen, Søren Højgaard, et al. "Large-scale electricity storage utilizing reversible solid oxide cells combined with underground storage of CO 2 and CH 4." Energy & Environmental Science 8.8 (2015): 2471-2479.

# How good can we get?

*Use water splitting as reference:*
- *Faradaic efficiency: 90%*
- *Over potential :0.3v*
- *Fuel cell efficiency: 70%*




Source: Zeng, Kai, and Dongke Zhang. "Recent progress in alkaline water electrolysis for hydrogen production and applications." *Progress in Energy and Combustion Science* 36.3 (2010): 307-326.

# Do we have enough space?

- Methanol Storage:
  - Seasonal storage for California: $1.1 \times 10^6$ ton, or $1.5 \times 10^6$ $m^3$

- $CO_2$ Storage
  - For California: 25 Bcf
- $CO_2$ can be stored in natural gas storage site
  - Natural gas storage has a lot parallelism with $CO_2$ underground storage. Non permeable cap, porous storage.
  - Working gas capacity in pacific region: 284 BCF as of Apr 29 2016
- Plenty of space, a feasible plan

Source: EIA, weekly natural gas storage report, http://ir.eia.gov/ngs/ngs.html

# Future Work

- Preliminary economics
  - Catalyst material can be quite expensive
  - $RbO_2$ growing on $TiO_2$ nanotube

# Thank you

QUESTIONS?