A Novel Modular Coal-to-Methanol Reactor Using Electroactive Membranes

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fundamentals | use-inspired basic research
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electrochemical science and technology
material synthesis | micro-fabrication | device design

electro-analysis | methods development | cross-disciplinary translation

Redox Flow Batteries

Alkaline electrolysis and fuel cells

Thermo-electrochemical catalysis
Reducing the C-intensity of chemical manufacturing still requires a lot of carbon and hydrogen…

Data from Schiffer and Manthiram *Joule* 2017, 1 (1), 10-14.
Opportunities from renewable (over)supply
Cheap electrons from renewables provide an opportunity to use carbon-rich feedstocks and sequestered CO$_2$ for value-added chemical production.
Hedging our bets...

Electrolytic hydrogen is an attractive alternative to fossil-derived hydrogen

PV/Wind

Surface or desal’ed water

\[ e^- \]

Electrolyzer

LP H\(_2\)

H\(_2\) storage & transport

HP H\(_2\)

thermal reactor

low-energy (oxidized) substrate
Hedging our bets...

Electrolytic hydrogen is an attractive alternative to fossil-derived hydrogen

We study this!
Hedging our bets...

*Process intensification*: radical decrease in process complexity, cost, and/or footprint by replacing several individual process units with one electrochemical reactor

We study this too!
Electrochemically Pumped Membrane Reactor
Linking thermal & electrochemical steps across a charge-conducting membrane

Inspiration: Photosynthetic CO₂ Fixation

1. Light is absorbed in chlorophyll and used to power photosynthesis
2. Enzymes extract electrons and H⁺ ions from water and transport them across the cell membrane
3. A separate set of enzymes uses electrons and H⁺ ions to convert CO₂ into sugars

Vision: a Chemical Industry Based on CO₂ Reuse

1. Renewable electricity is fed to a catalytic assembly that extracts electrons and H⁺ ions from water and injects them into an inorganic membrane
2. A second catalyst uses the electrons and H⁺ ions to convert CO₂ into methanol
3. Methanol can be used to create an array of fuels and commodity chemicals

Also see work by Surendranath, Berlinguette, CoorsTek, and others

image credit: J. McKone & Rick Henkel
Wish list:

1. Inorganic proton-electron conductor, stable under reducing conditions and elevated T
2. Congruent oxide redox reactivity under thermal and electrochemical conditions
3. Low barrier to electrochemical oxide hydrogenation
4. Facile H (reverse) spillover to thermal hydrogenation catalyst
5. Ability to tune reactivity of hydrogen within oxide phase to match reactant
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Transition metal hydrogen bronzes
\[ H_xMO_y \]
(M = Ti, V, Mo, etc.)
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H-spillover and H-intercalation
classical pictures imply different pathways

Dynamics of hydrogen uptake and diffusion
Imaging lateral H migration via $H_xWO_3$ “fronts”
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Dynamics of hydrogen uptake and diffusion

H-front migration rates imply single mechanism

Initial migration rate is constant and **way too fast** to be gated by H\(^+\) (or H atom) diffusion!
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Using quantum chemistry to predict bronze PCET thermochemistry

Regression models: trained on DFT-predicted acid/base properties on subset of H-locations in $H_xWO_3$
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Oxygens are basic

Metals are acidic

Correlation coefficients for DFT-predicted energy (related to $E^o$) vs DFT-predicted acid/base properties
Using quantum chemistry to predict bronze PCET thermochemistry

**DFT + regression models**: greatly decrease computational cost for convex hull calculations

**Important feature of $H_xWO_3$**: fast reduction but severely inhibited oxidation

Collab w/ G. Mpourmpakis
Using quantum chemistry to predict bronze PCET thermochemistry

Model is highly extensible: input requires only reactant oxide crystal structure
Chemical Looping Hydrogenation

Electrochemical properties of $H_xWO_3$ allow us to predict how it will behave in a looping configuration.

Model reaction: acetylene hydrogenation
Chemical Looping Hydrogenation
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**Cyclic voltammogram**

- CAN hydrogenate
- CANNOT hydrogenate

**DFT calculations**

Both results suggest that $H_xWO_3$ will hydrogenate $C_2H_2$ and $H_xV_2O_5$ will not
Chemical Looping Hydrogenation

Predictions validated: HxWO3 hydrogenates acetylene and HxV2O5 does not

**WO₃**

- **C₂H₂ conversion**
- **C₂H₄ selectivity**
- **C₂H₆ selectivity**
- **C balance**

**V₂O₅**

- **C₂H₂ conversion**
- **C₂H₄ selectivity**
- **C₂H₆ selectivity**
- **C balance**

**ALSO:** note product distribution – ethylene is primary C2 product
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Electrochemically pumped syngas-methanol

Applied voltage to increase chemical potential of hydrogen

(a) $\text{H}_2$ activation via H-spillover

CO, H$_2$, CO$_2$, H$_2$O $\rightarrow$ H$_*$$\rightarrow$ CH$_3$OH, H$_2$O

(b) CO hydrogenation using solid-state H

$\text{H}_x\text{WO}_3$
Electrochemically pumped syngas-methanol

Applied voltage to increase chemical potential of hydrogen

(a) H₂ activation via H-spillover

CO, H₂, CO₂, H₂O → H₂

CH₃OH, H₂O → CO, CO₂, H₂O

(b) CO hydrogenation using solid-state H

HₓWO₃

Open Circuit Potential of CO₂ - N₂ and CO₂ - H₂ Cells

Potential (V vs ref)

Time (s)
Final thought: electrochemical intensification

Are there circumstances under which heat and electricity together can enhance catalytic reactivity more than either can individually?
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