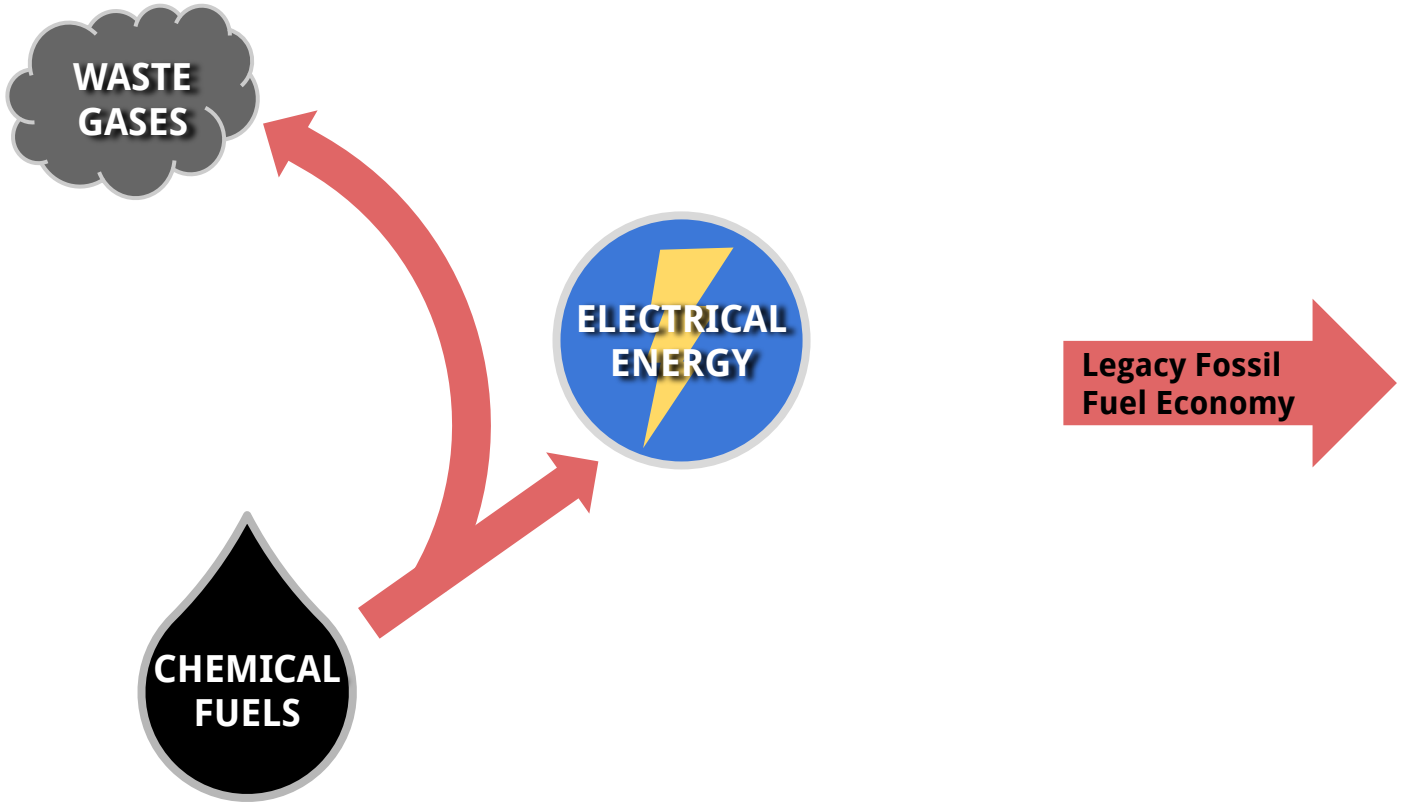
Sustainable Routes to Electrosynthesis of Industrially Valuable Small Molecules

Jo Melville
Thesis Defense

Surendranath Group
5/13/2021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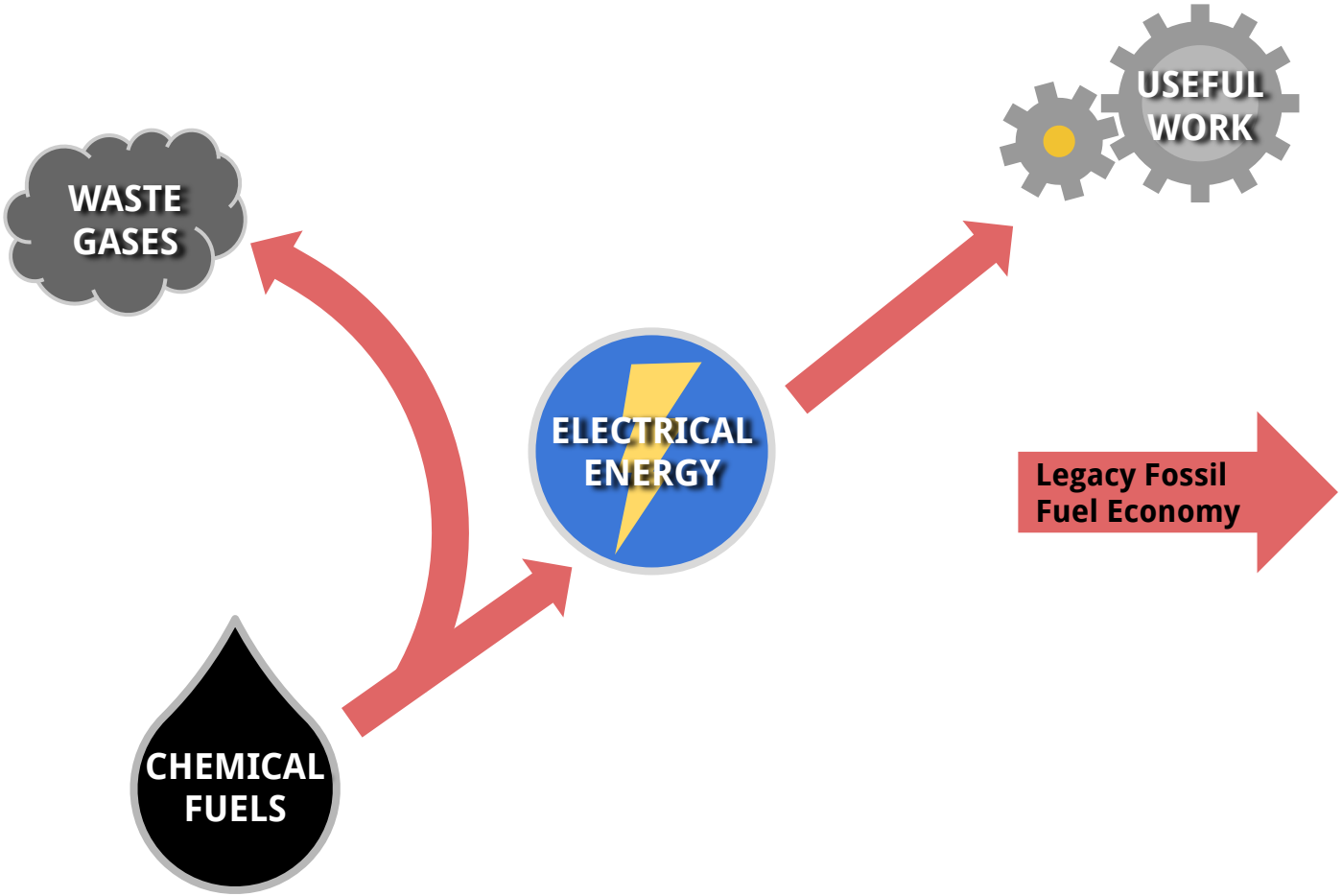
ELECTRICAL ENERGY
Legacy Fossil Fuel Economy
CHEMICAL FUELS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USEFUL WORK
ELECTRICAL ENERGY
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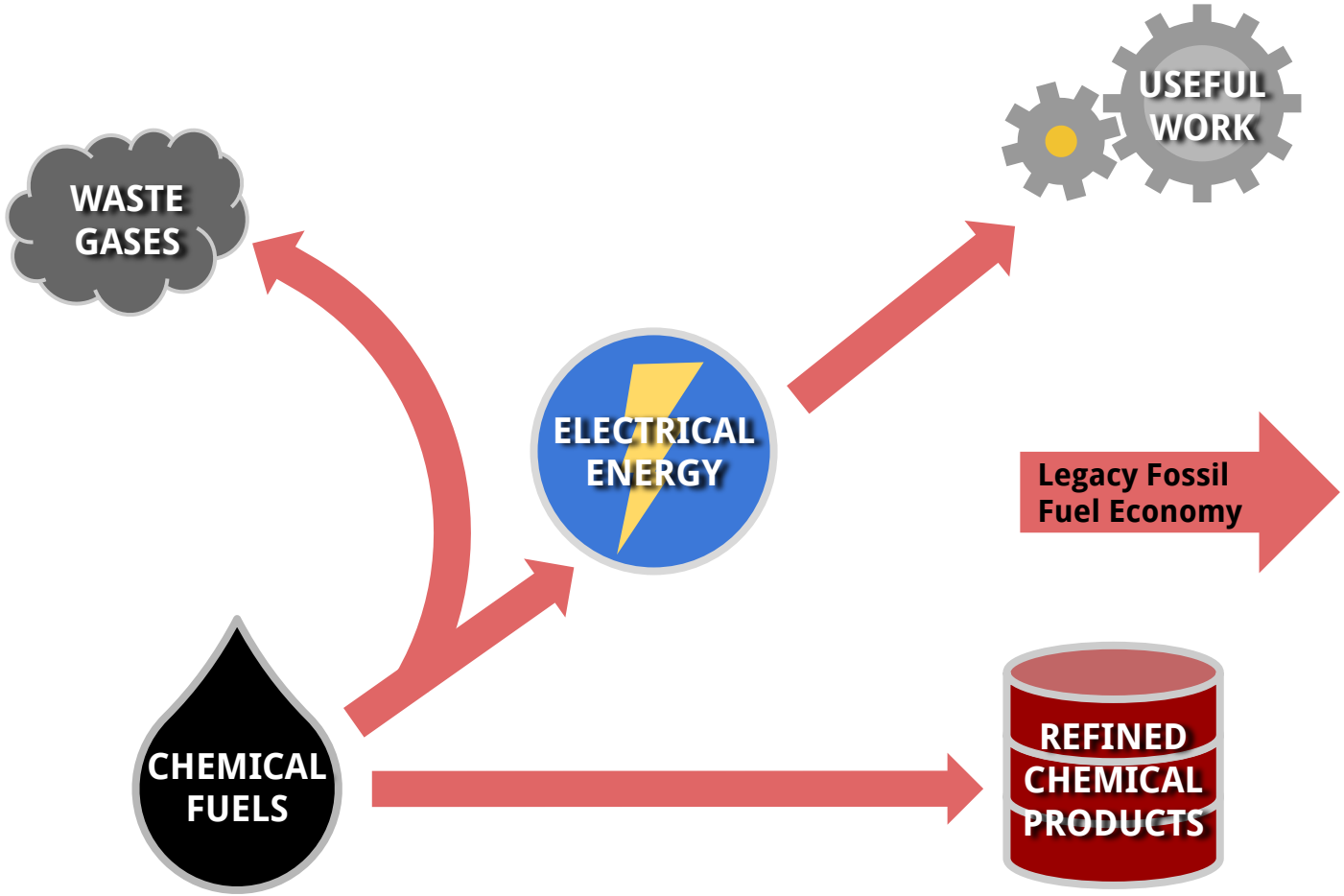
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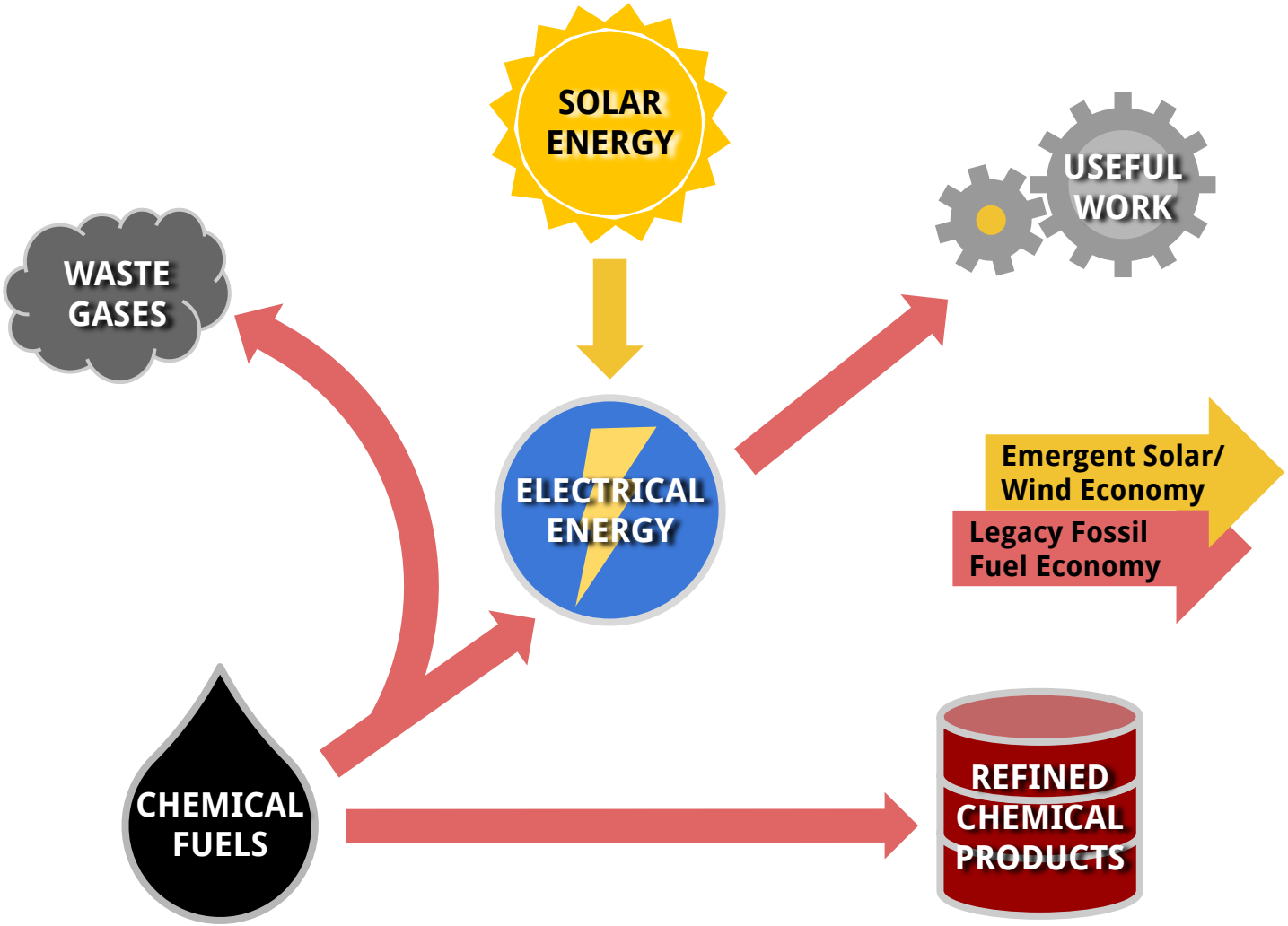
CHEMICAL FUELS
REFINED CHEMICAL PRODUCTS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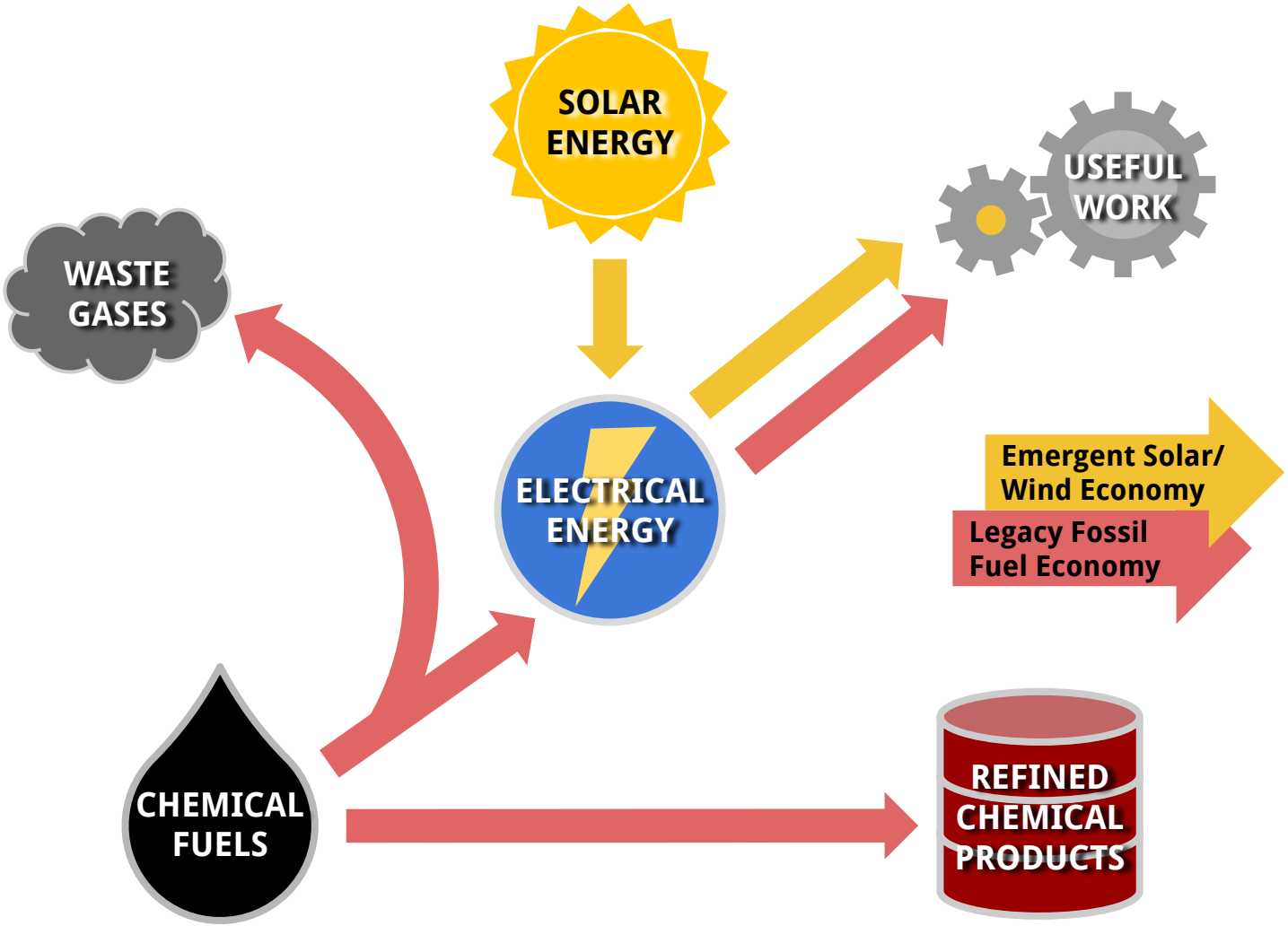
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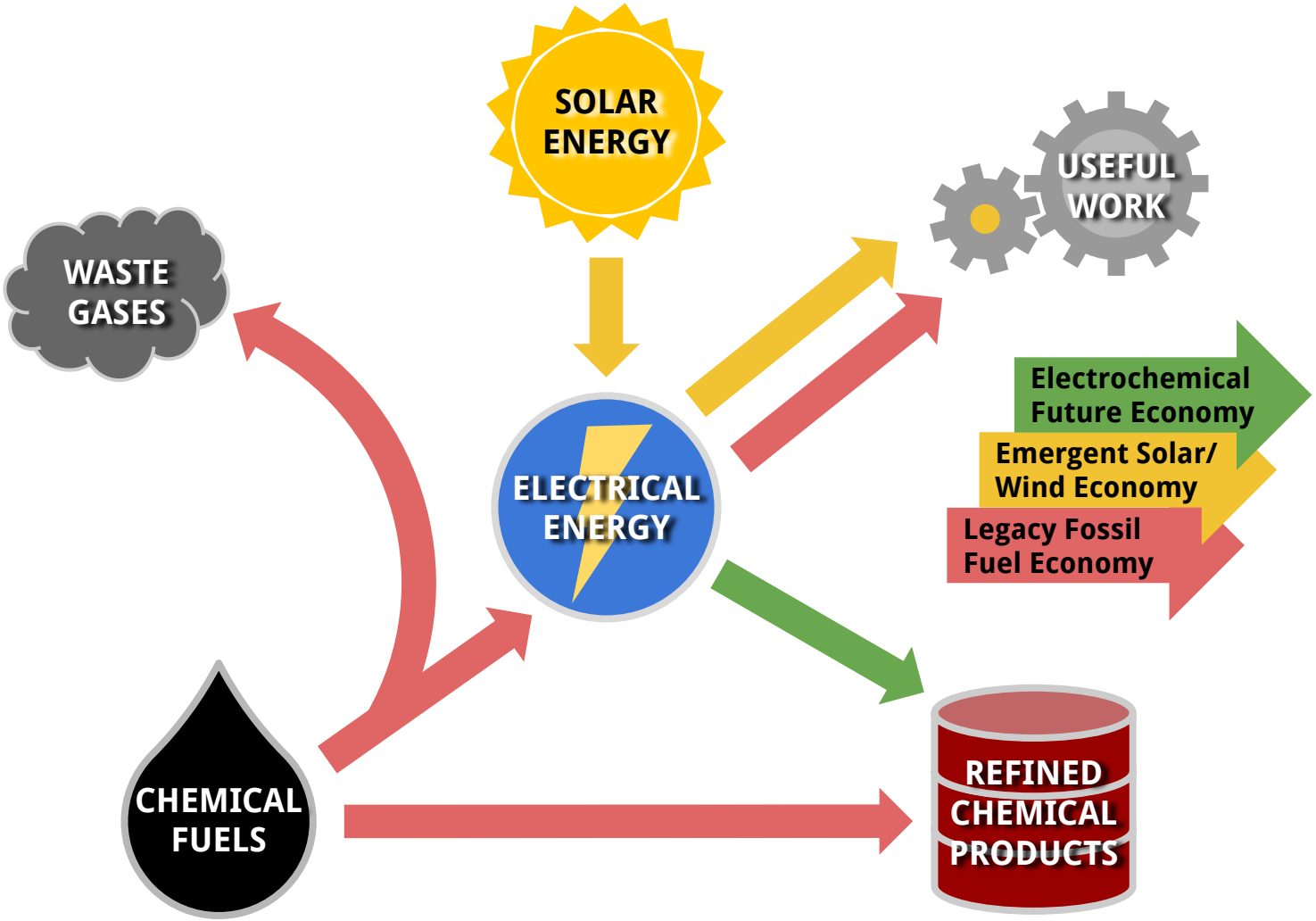
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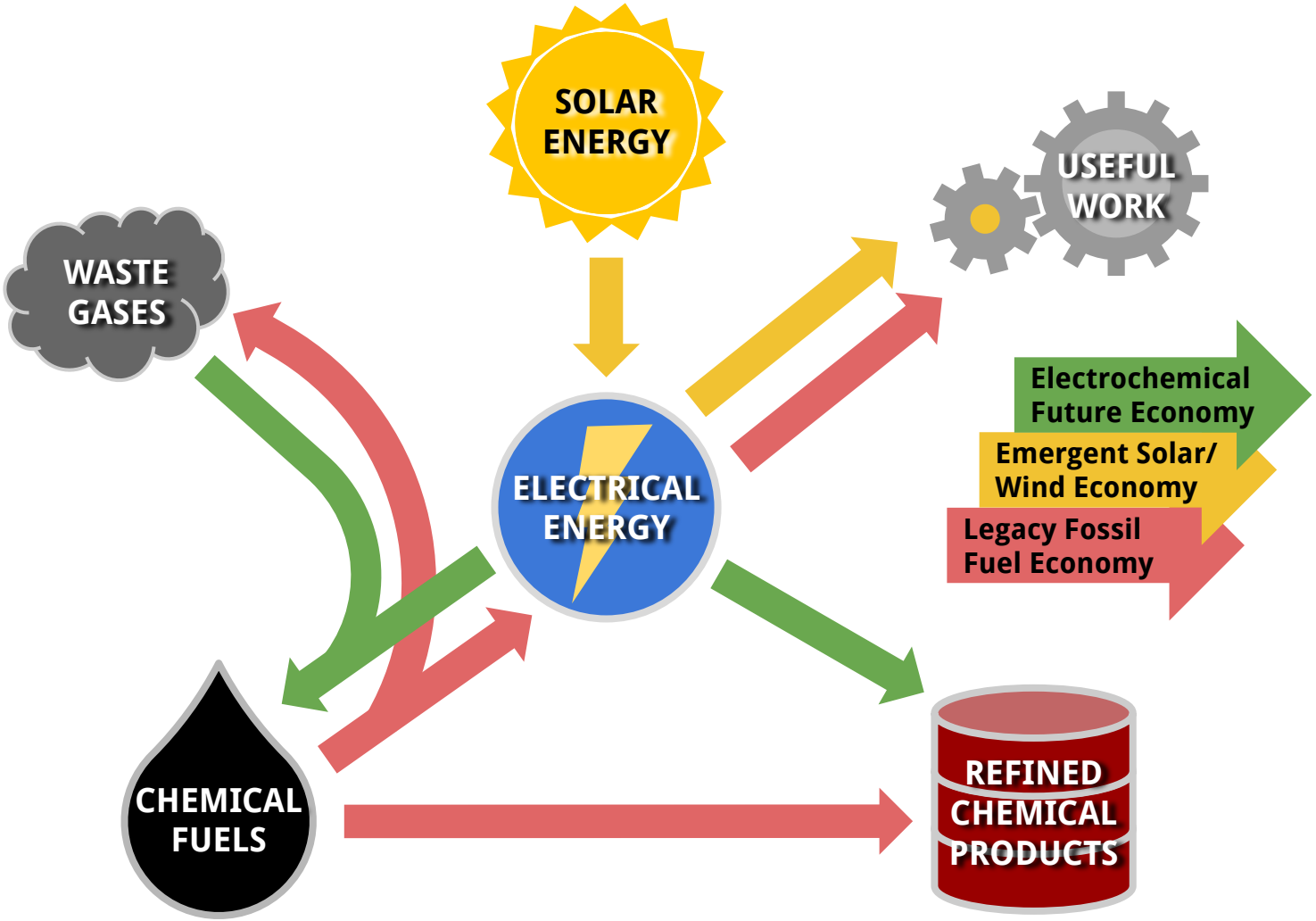
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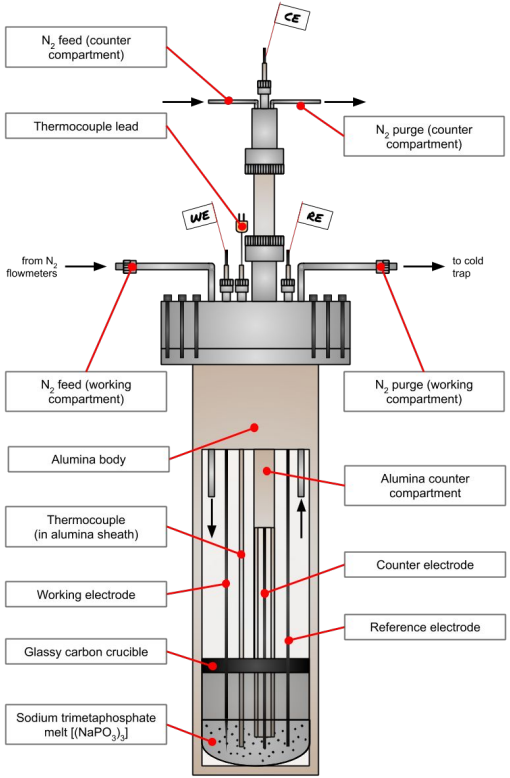
Short-Circuiting the Phosphorus Economy

the central role of P_4

Reduction of Molten $[NaPO_3]_n$ to P_4



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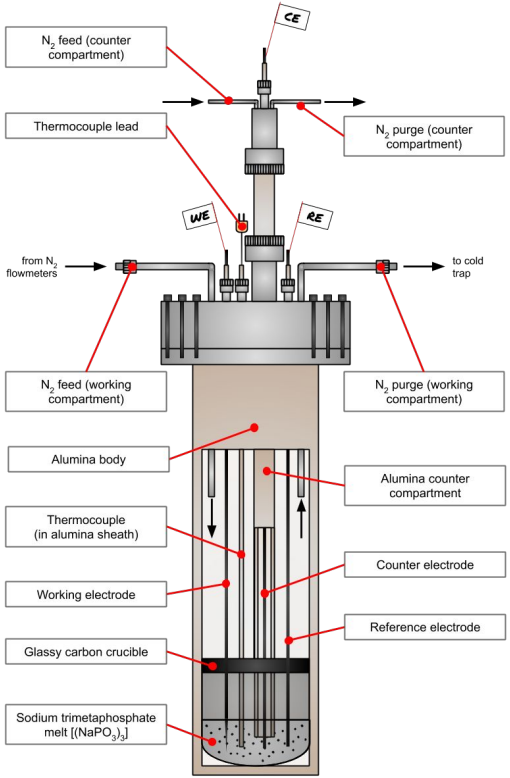

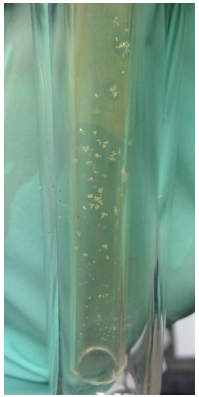

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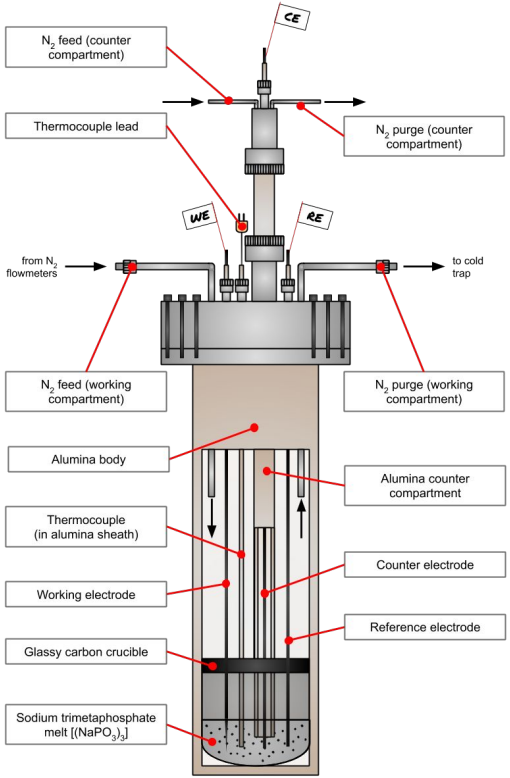

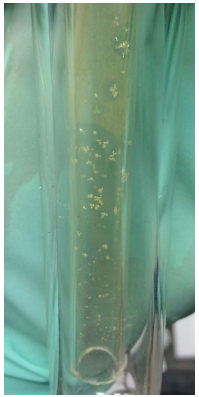

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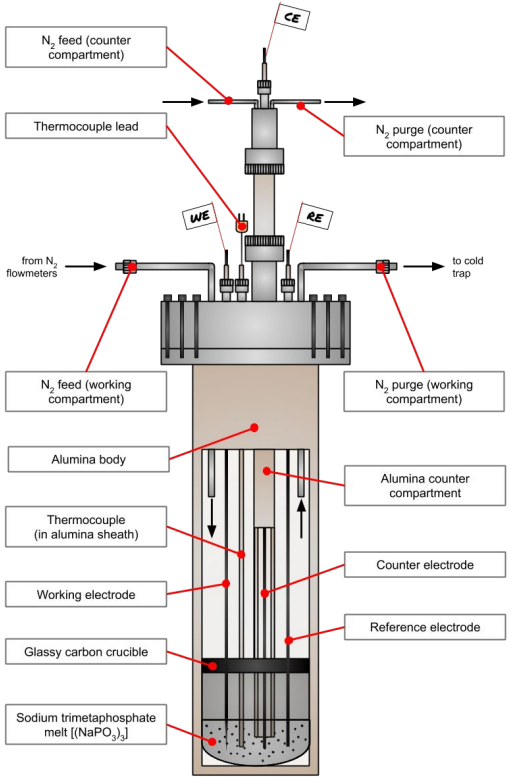

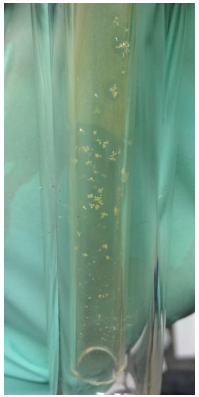

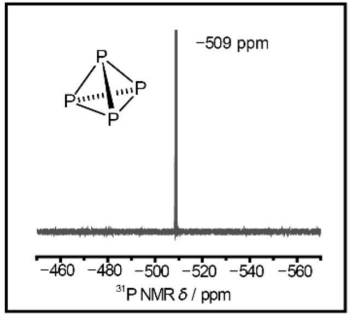

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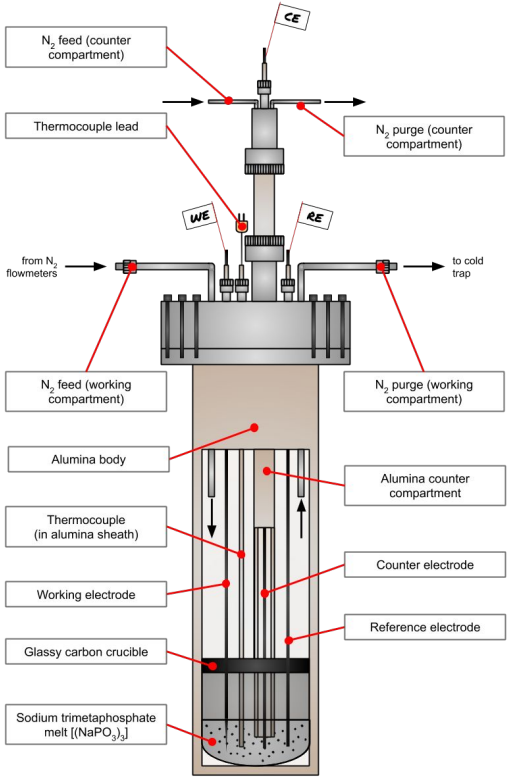

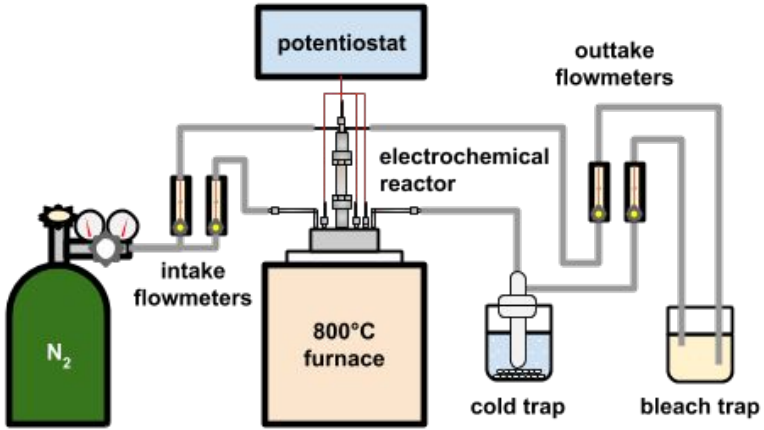

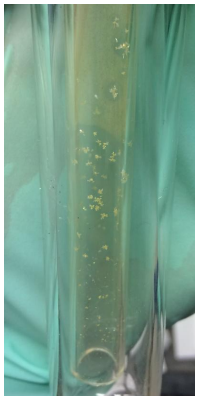

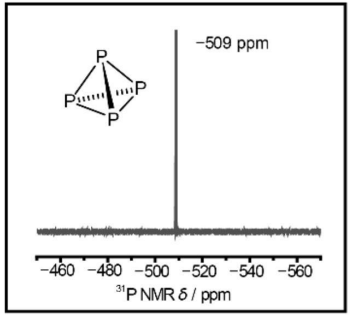

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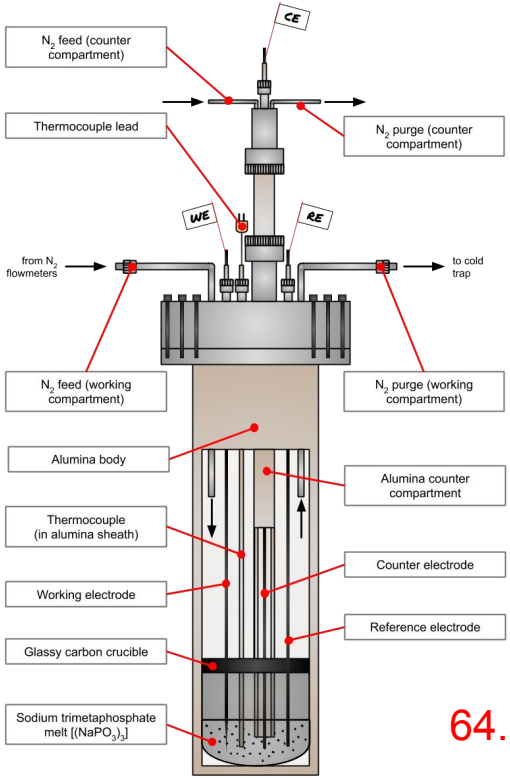
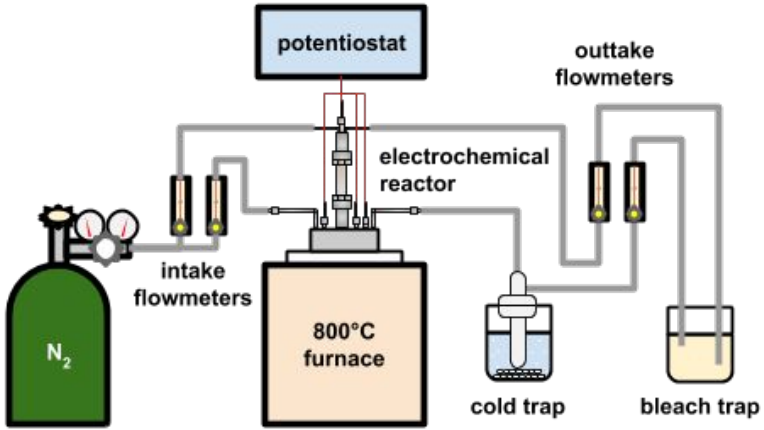
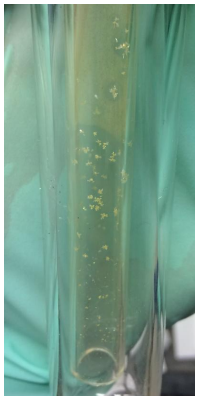
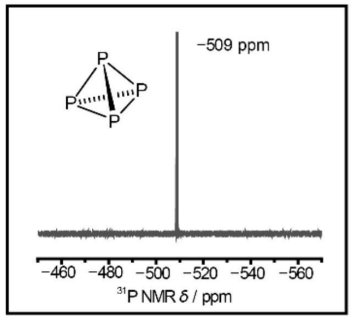




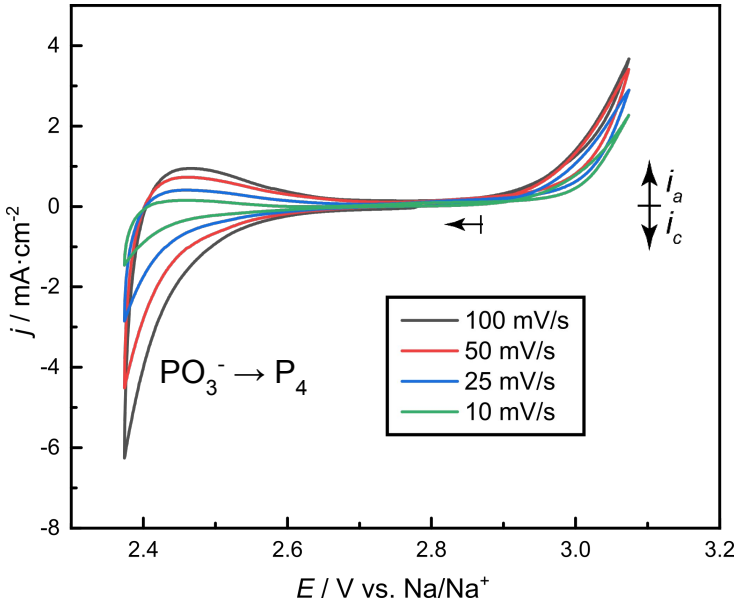




Peak FE: 95%

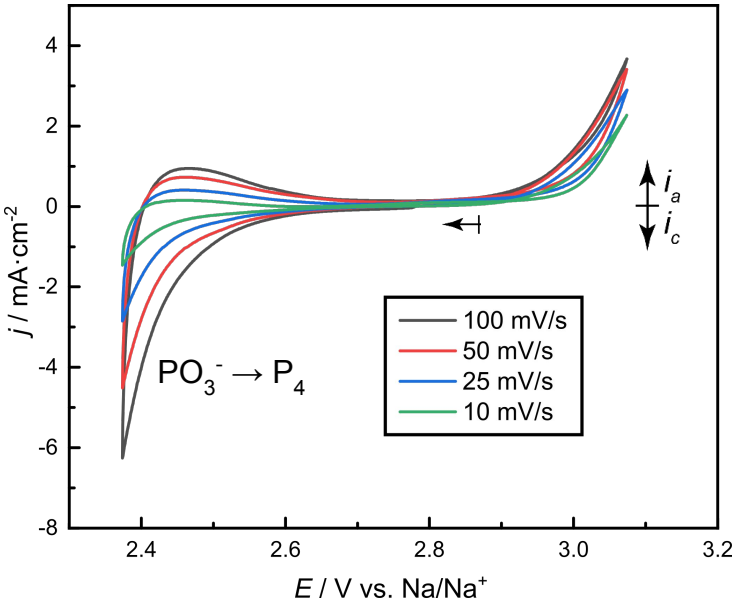
64.5% observed out of 68% gas flowthrough

Determining PRR Overpotential



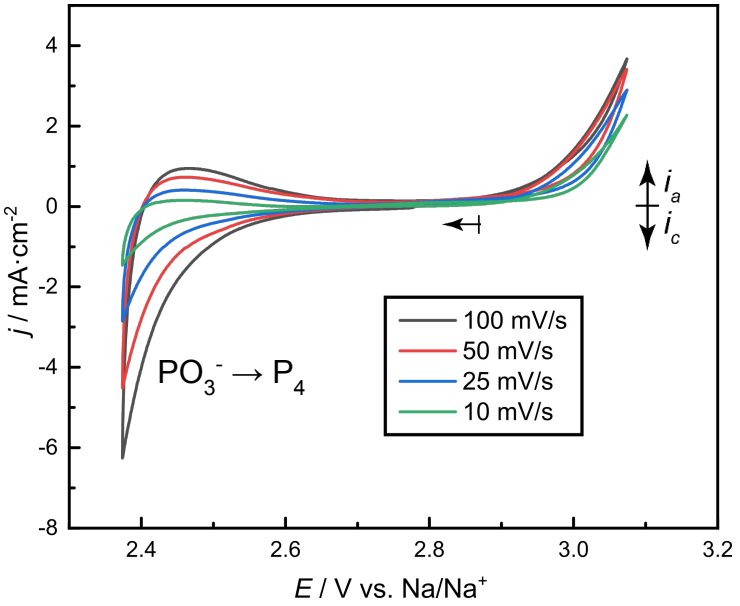
Determining PRR Overpotential

- Need E° to determine η



Determining PRR Overpotential

- Need E° to determine η
  - No theory or lit estimates, must determine empirically



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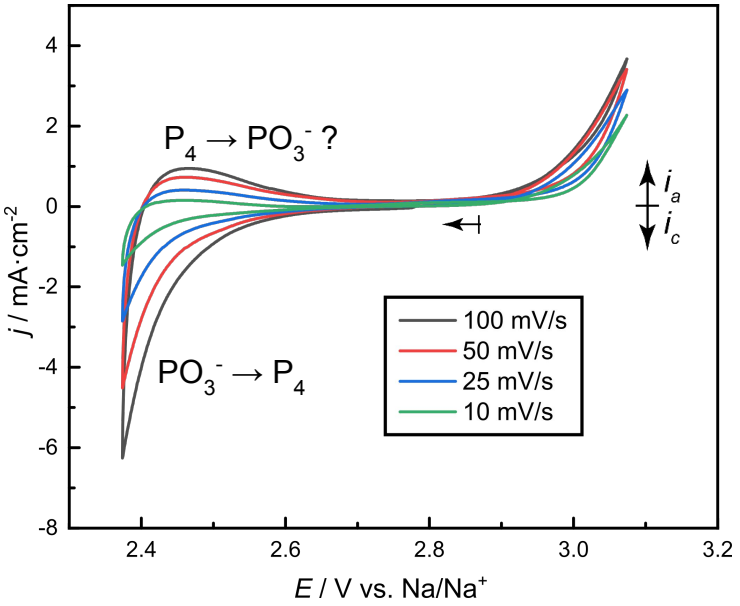

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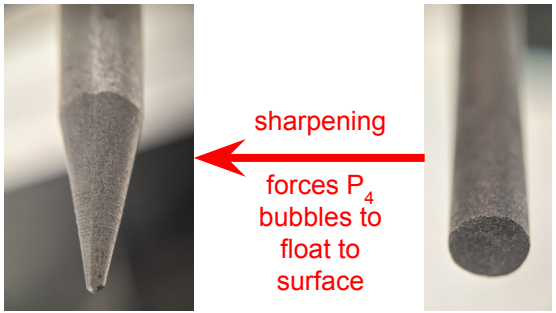

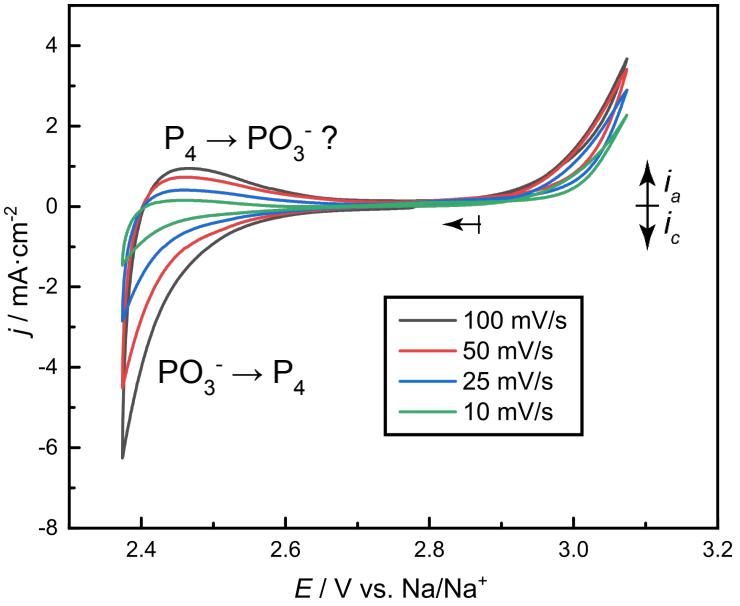

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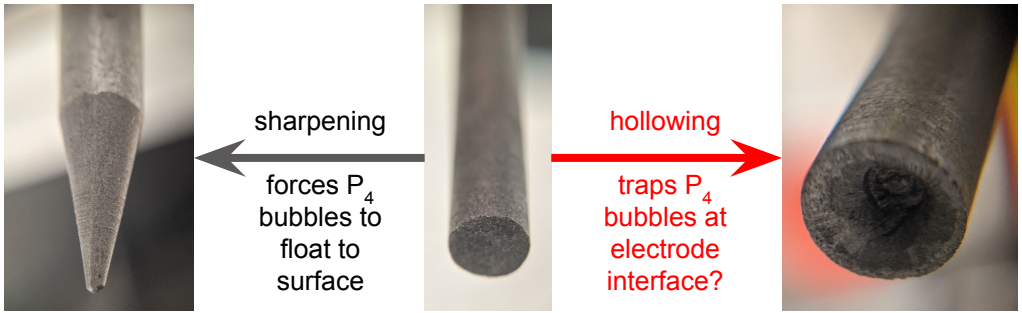
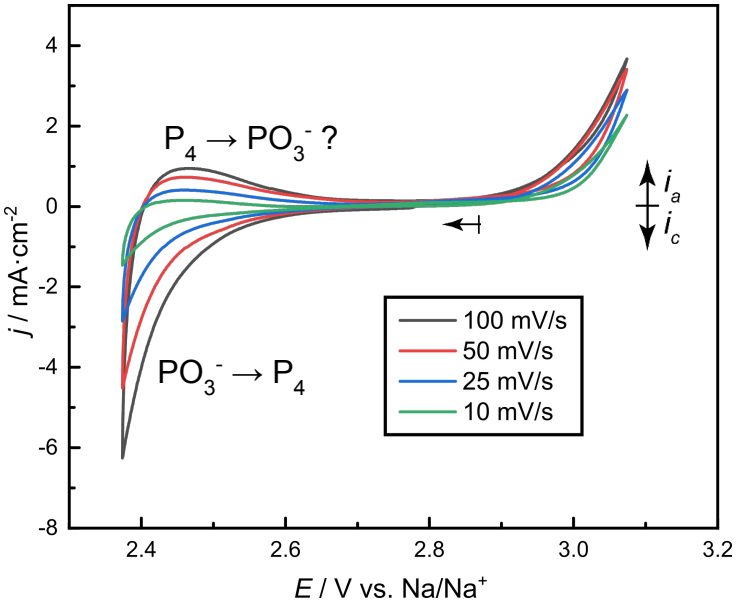
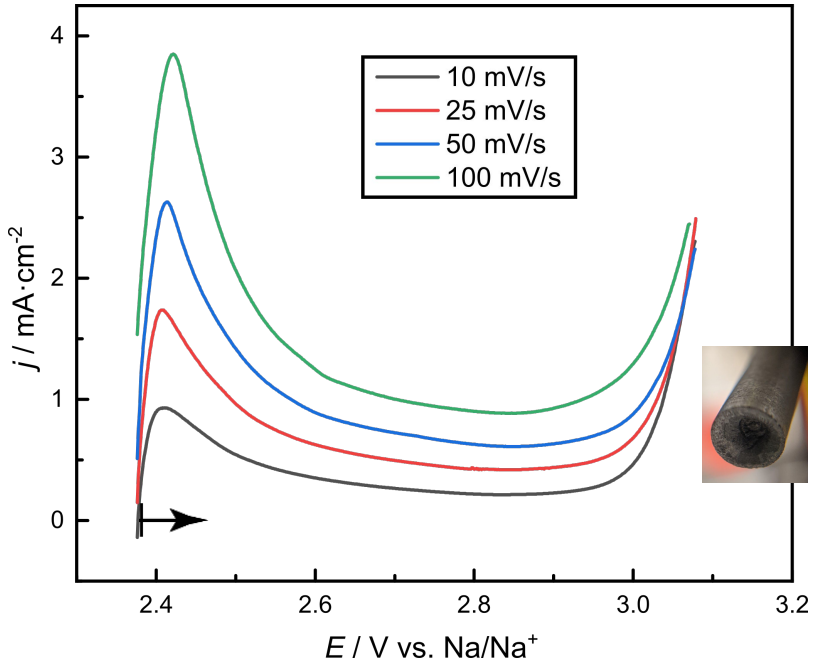




Hollowed Electrode Enables P_4 Trapping



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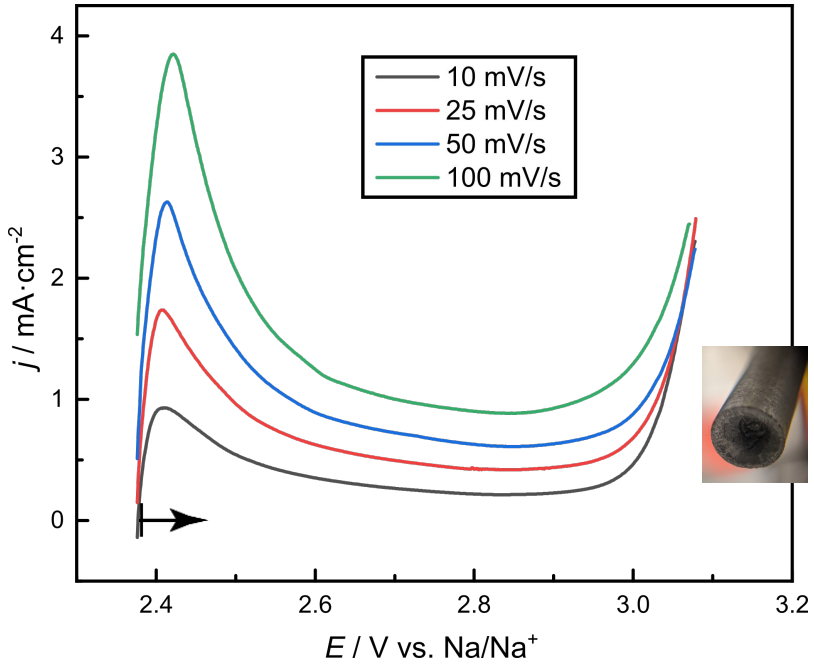
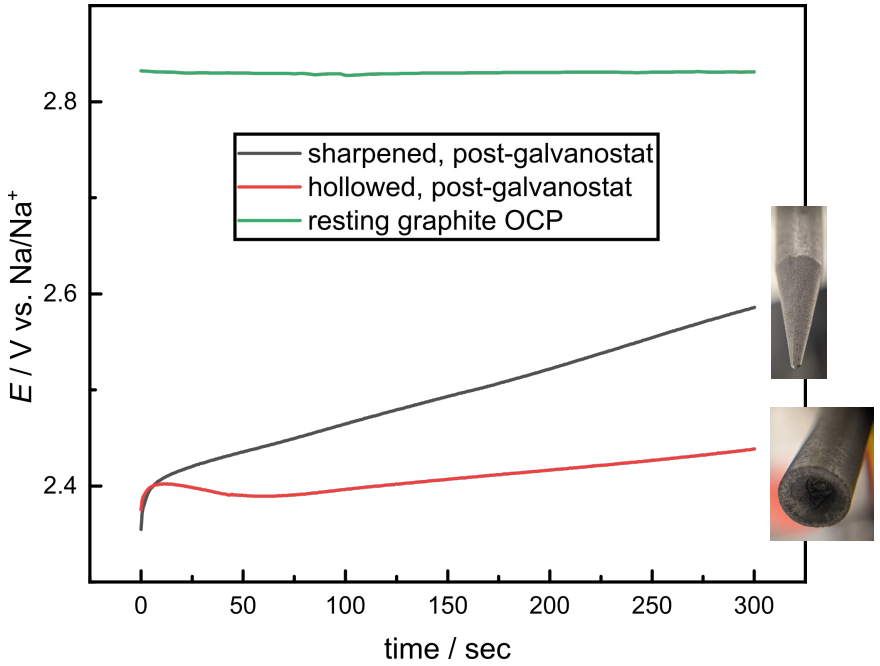
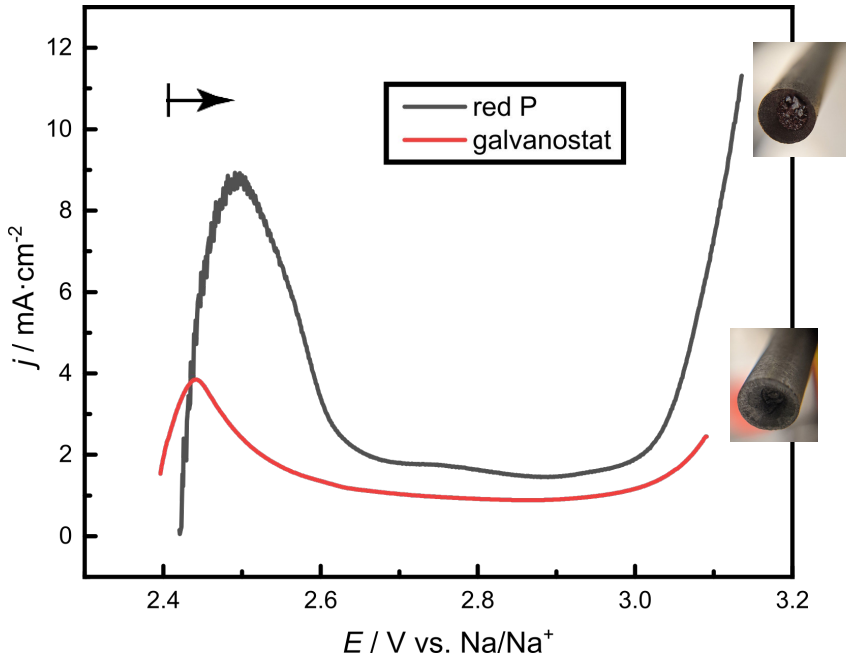
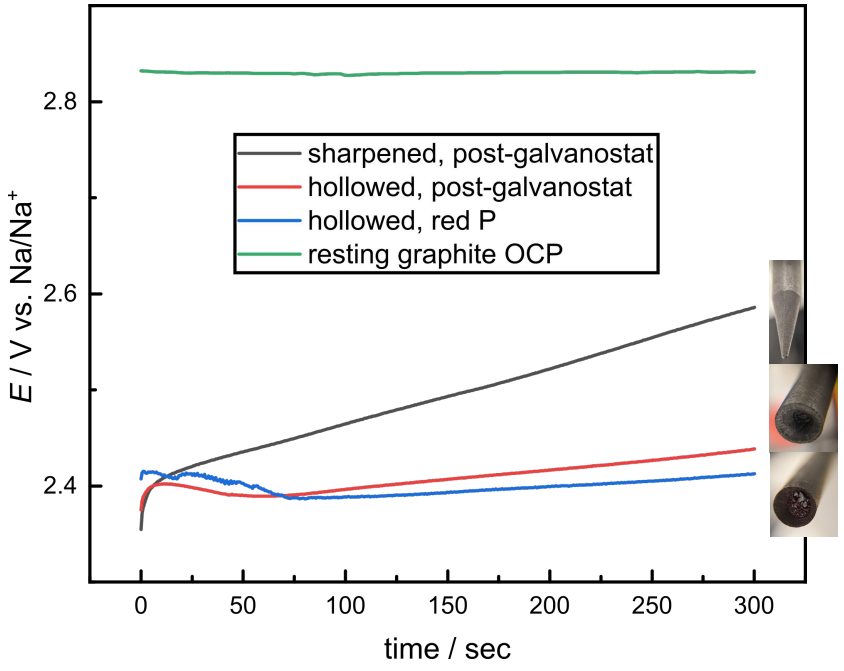


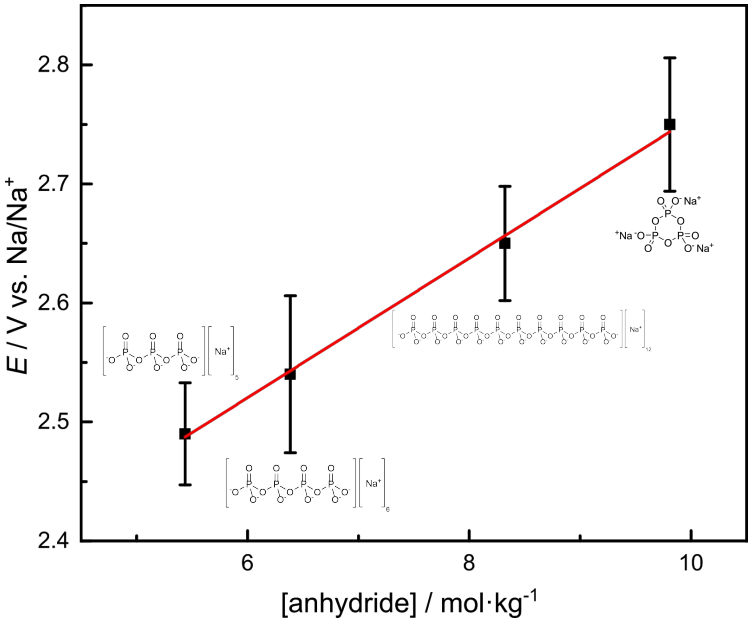


Product Dosing Confirms P_4 Potential





Anhydride Dependence of PRR



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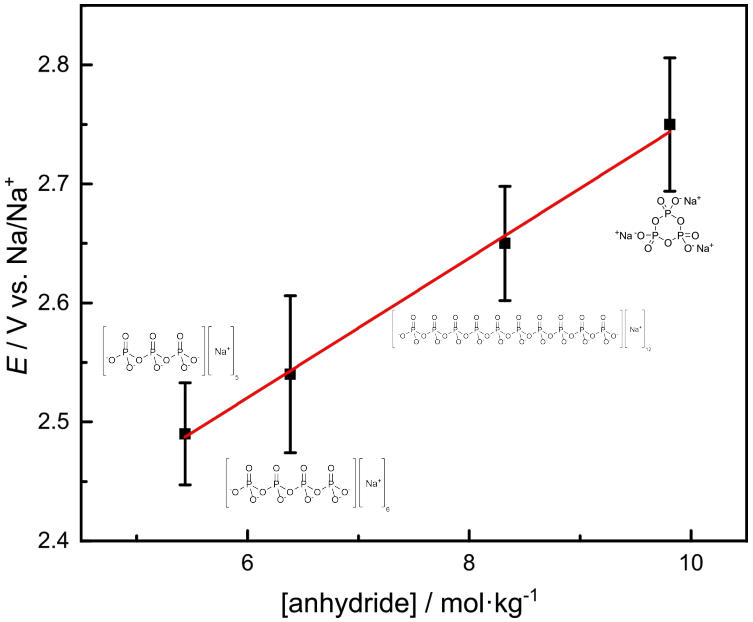

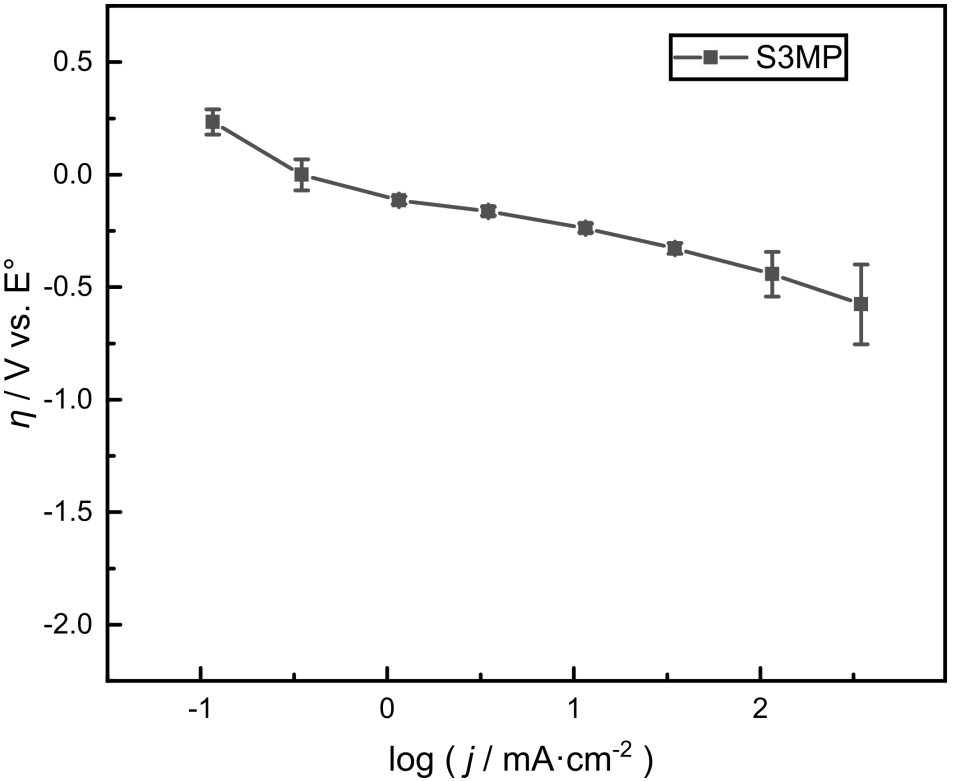

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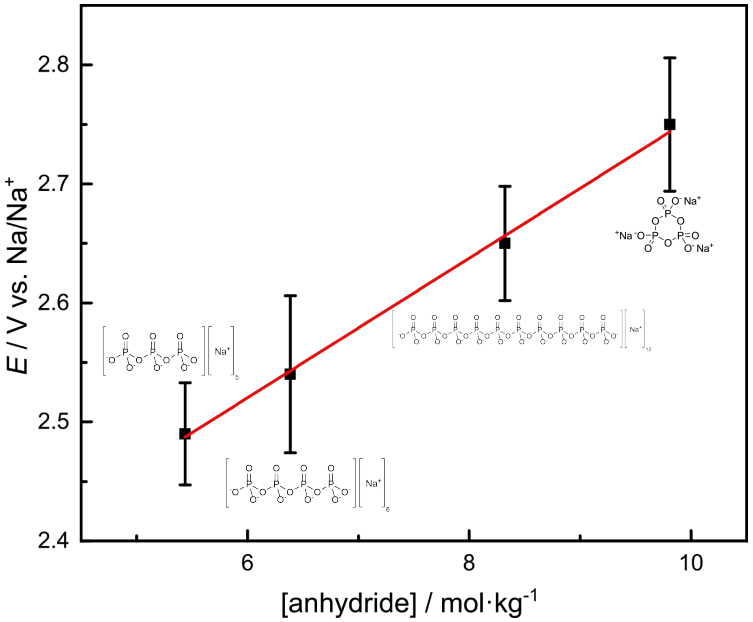

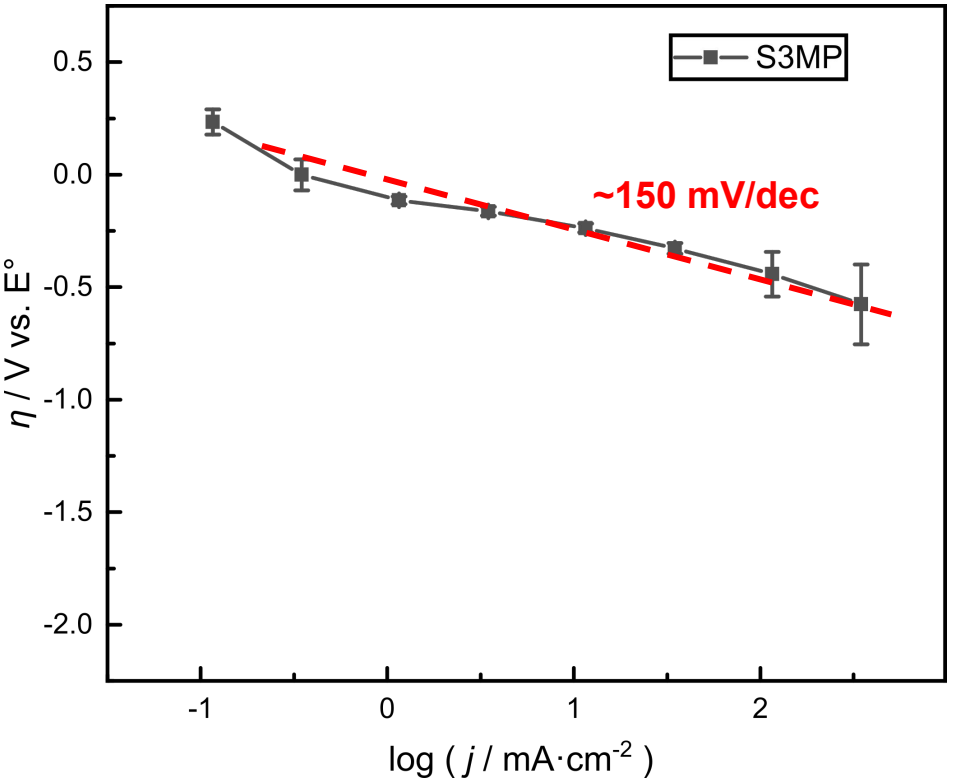

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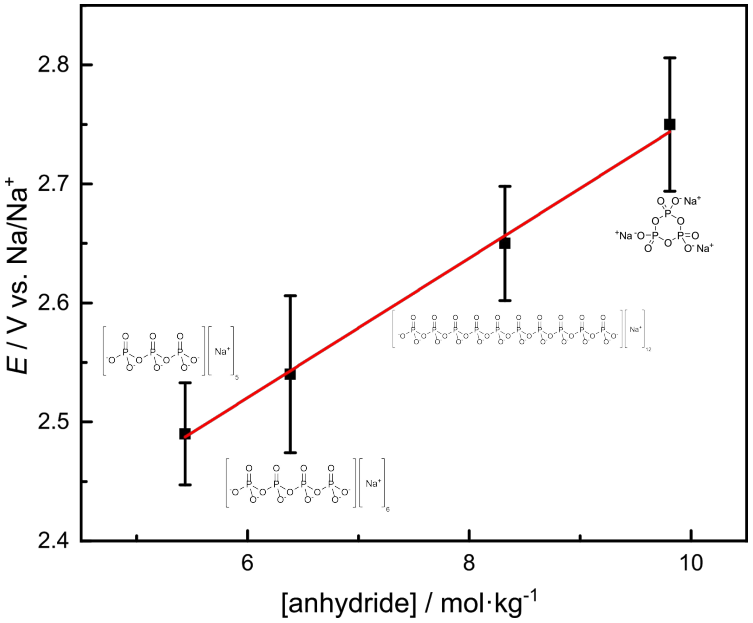
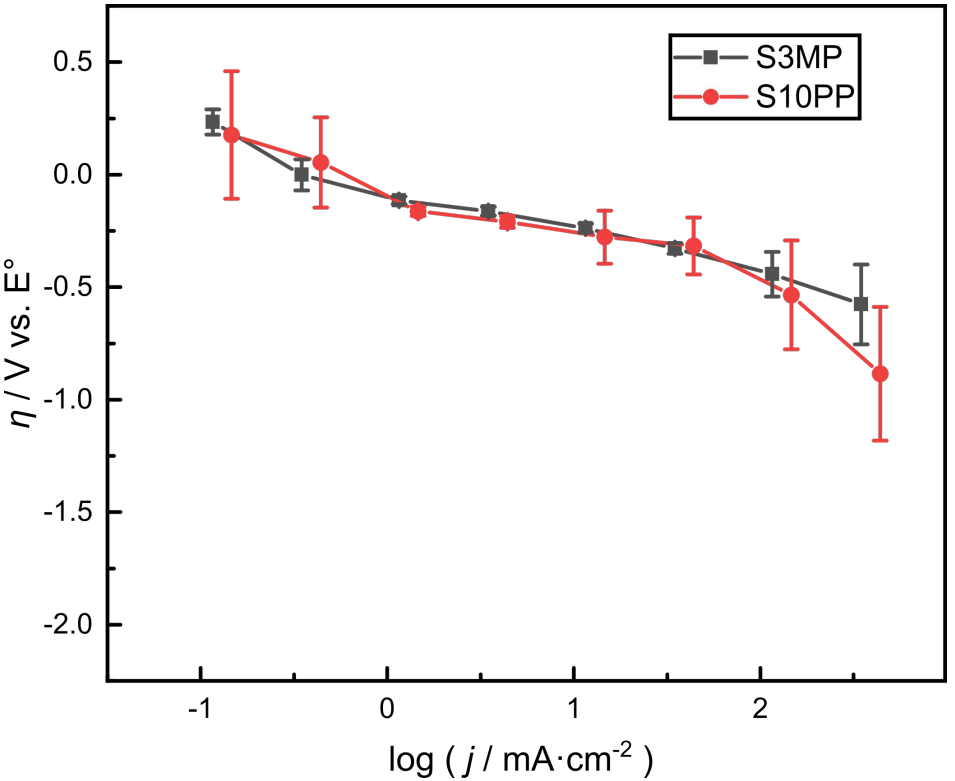
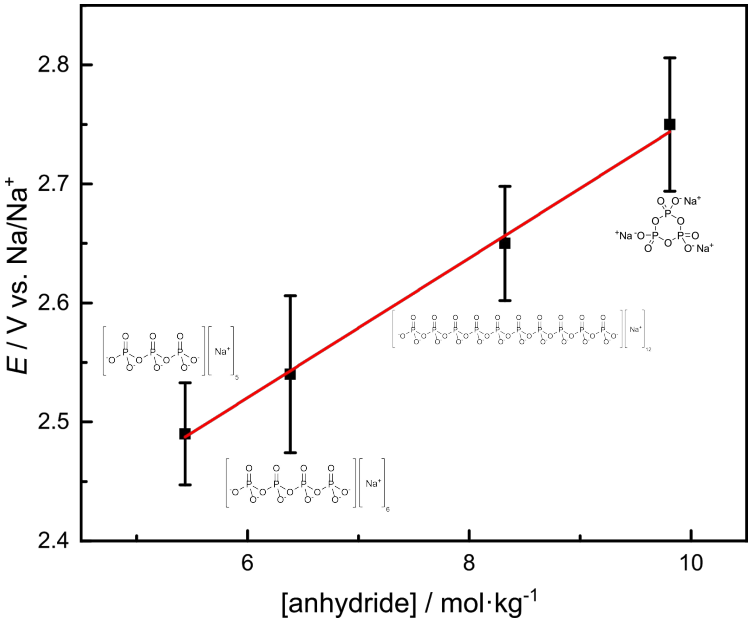
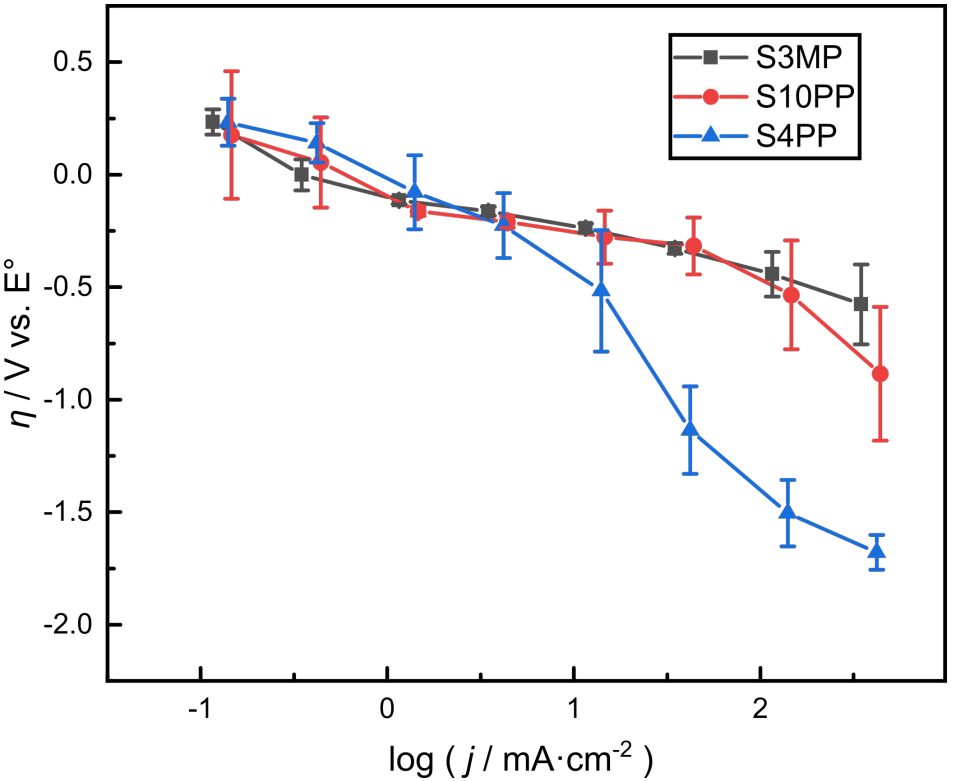




η Increases as [anhydride] Depletes





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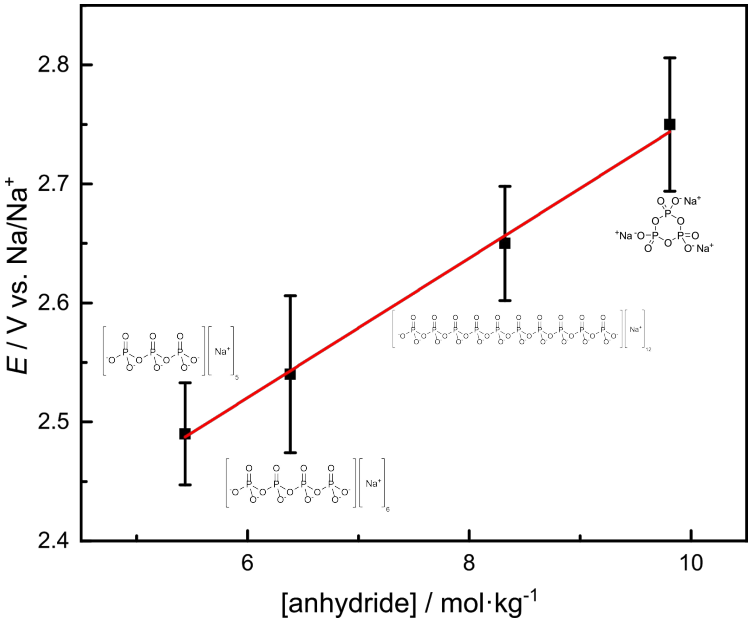
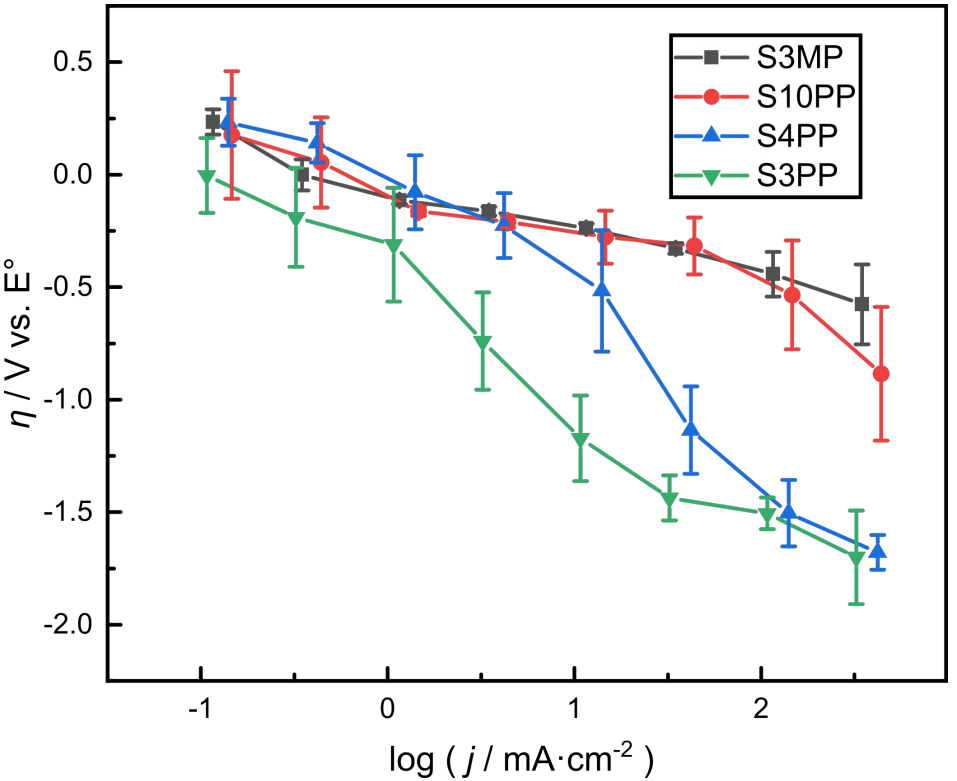
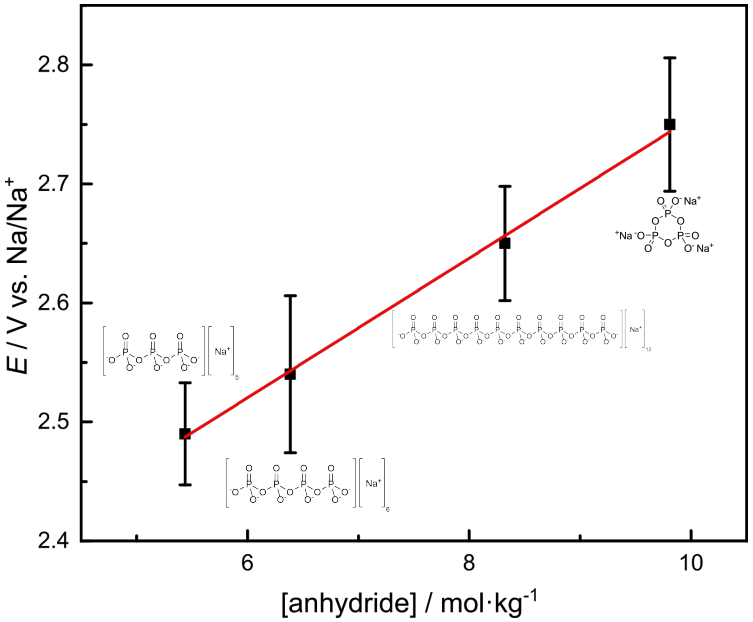
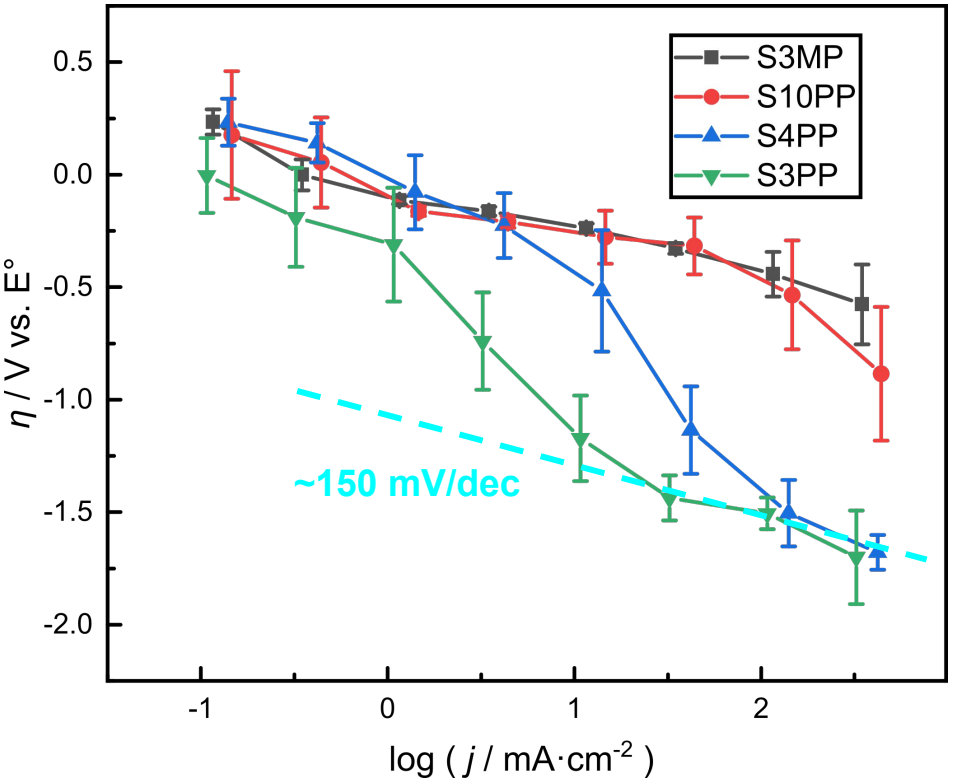


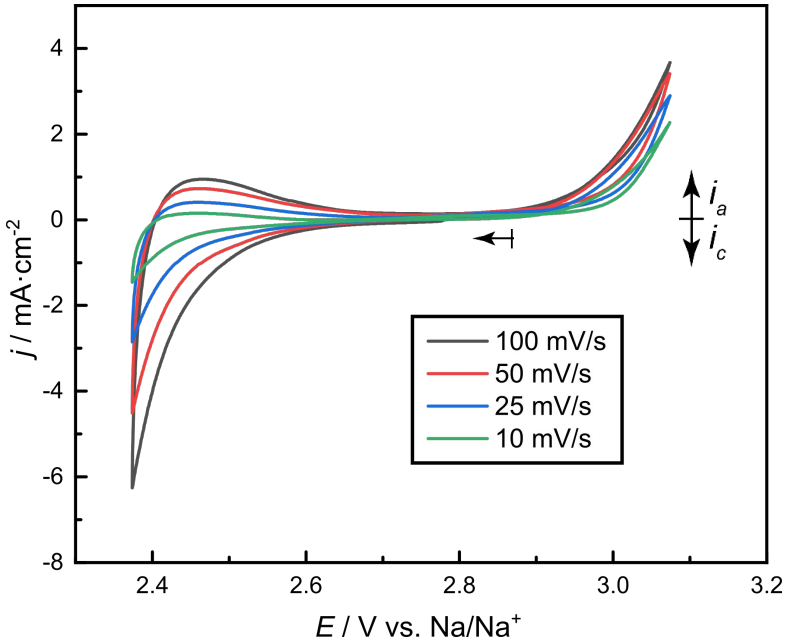


Tafel Curves Shift at Low [Anhydride]



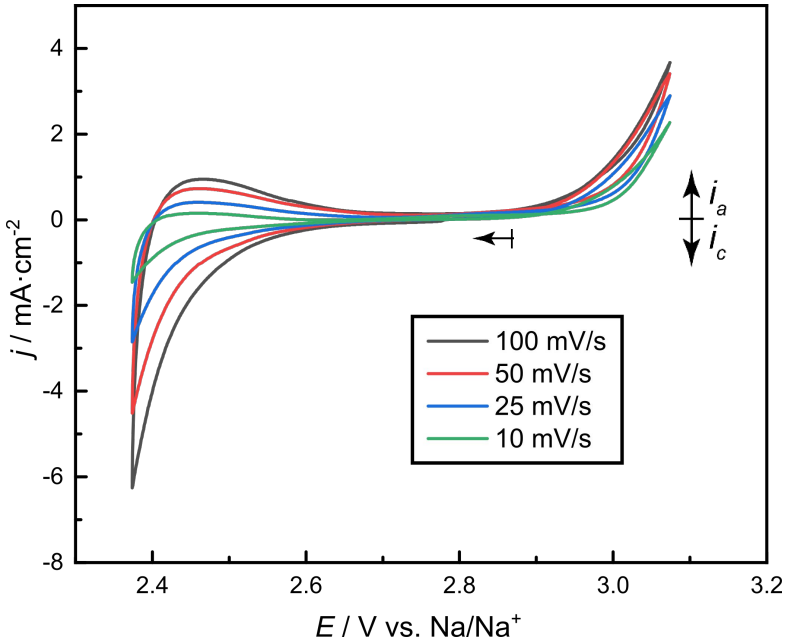


Simulations Accord EEC Mechanism



observed CV

Simulations Accord EEC Mechanism



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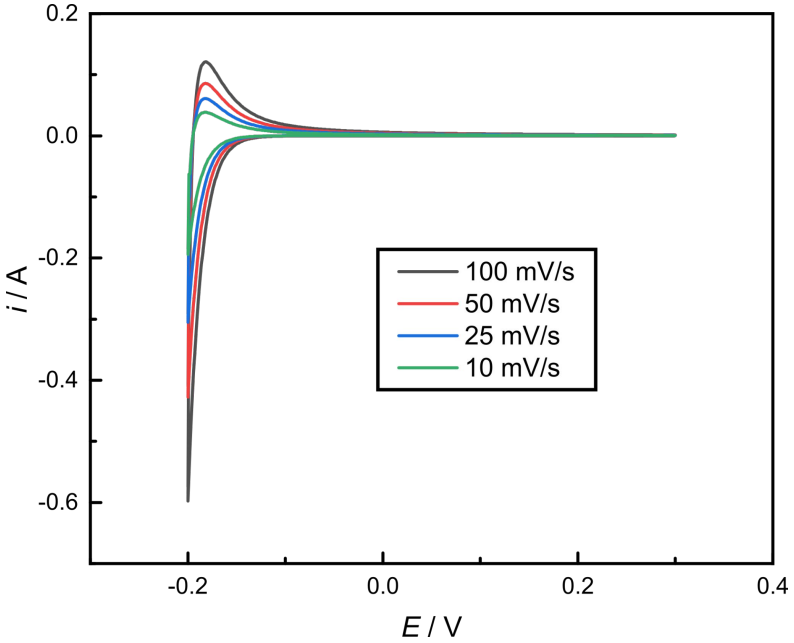

simulated CV

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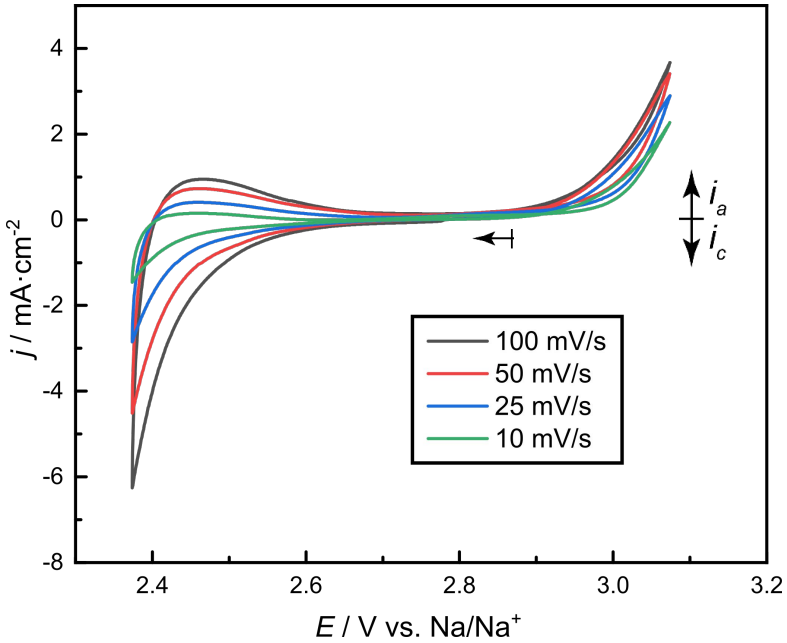

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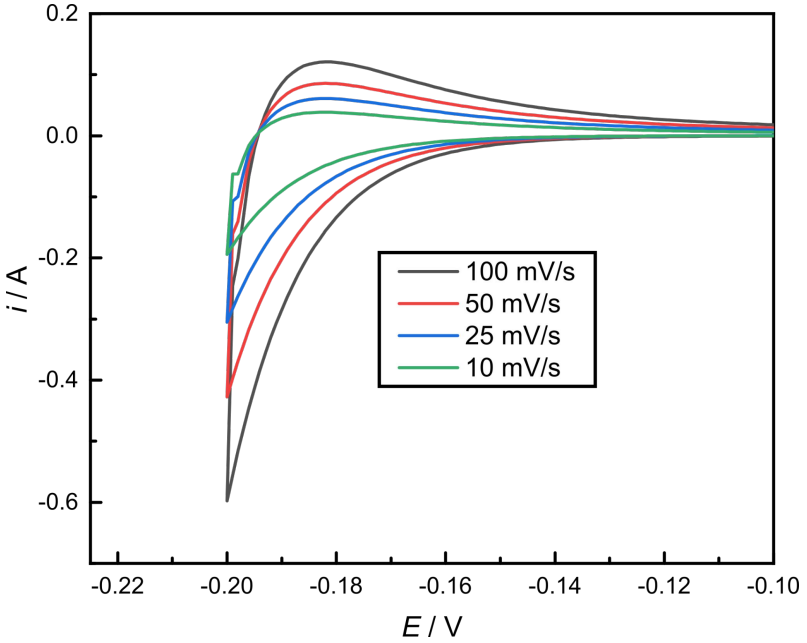
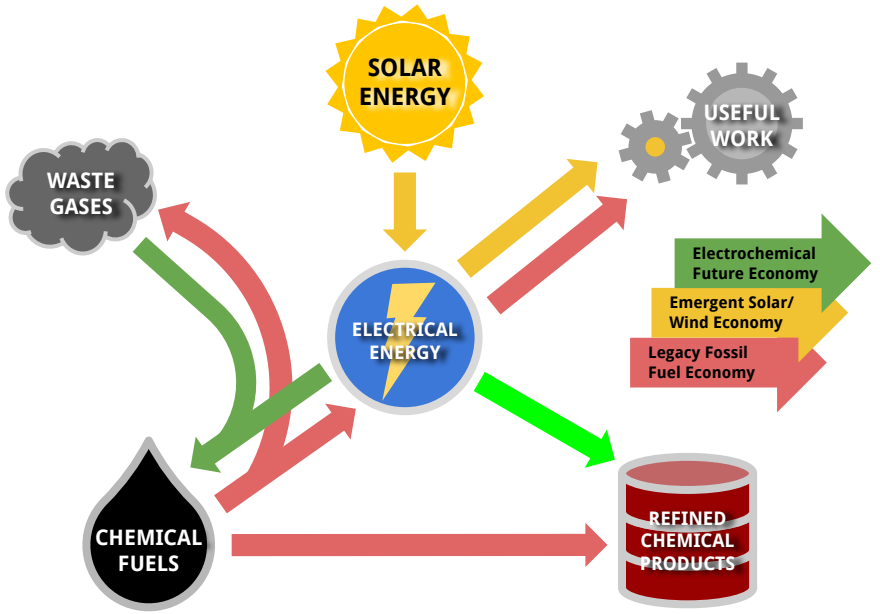


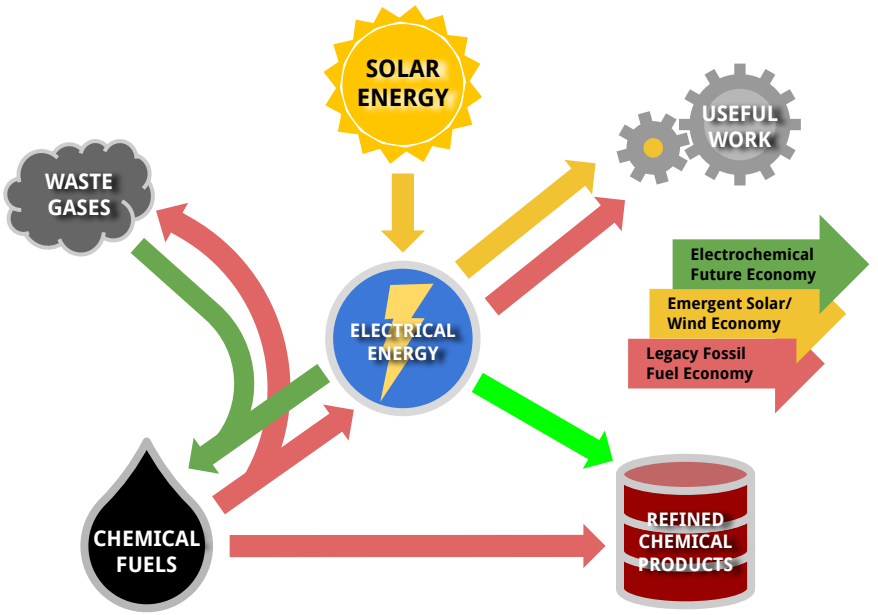
simulated CV

Conclusions & Outlook



Conclusions & Outlook

- Electrochemical PRR is extremely efficient



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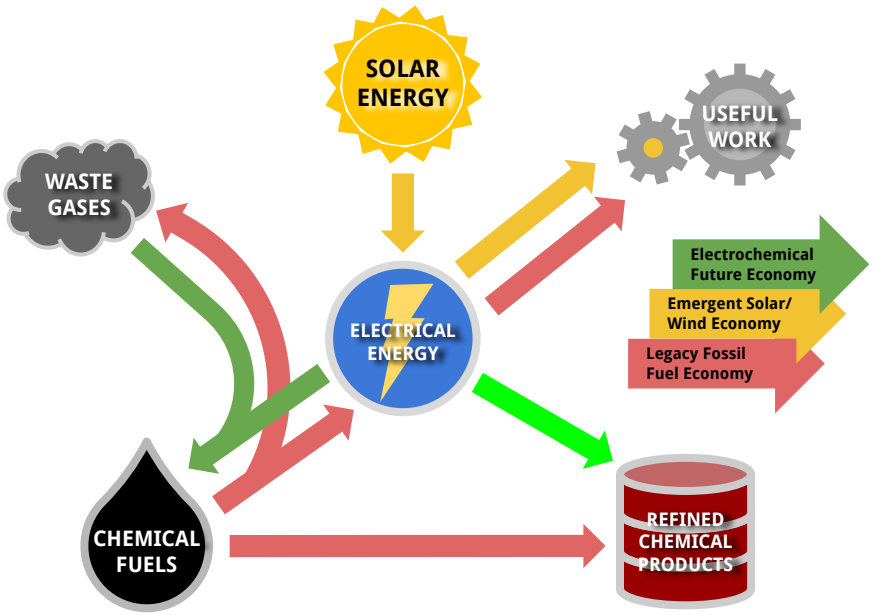
  - Near 100% atom and energetic efficiencies



Conclusions & Outlook

- Electrochemical PRR is extremely efficient
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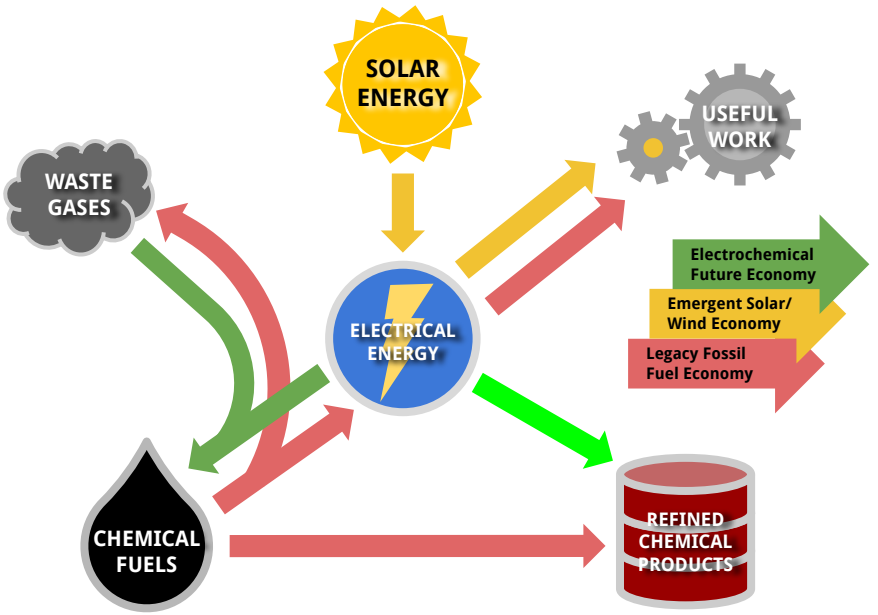
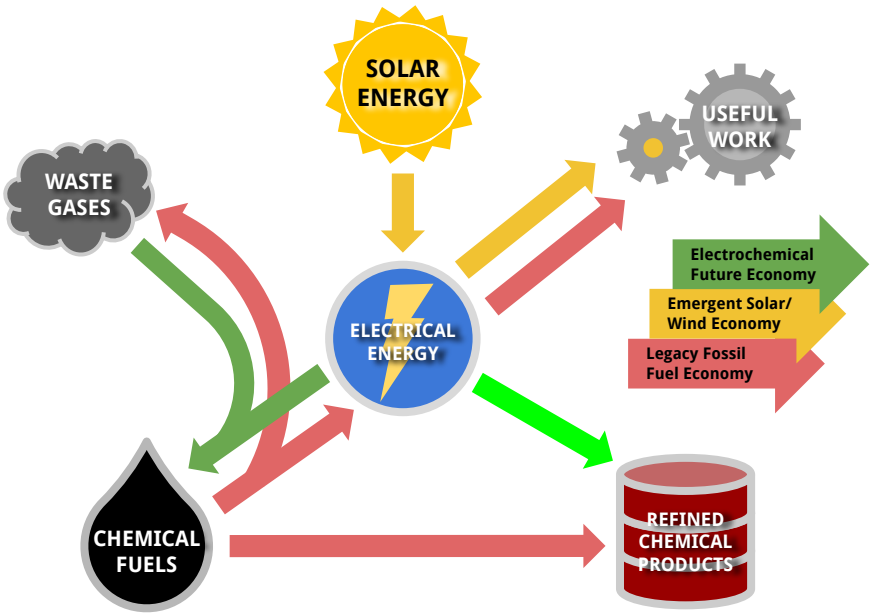
- Milder than incumbent process (1500 °C)



Conclusions & Outlook

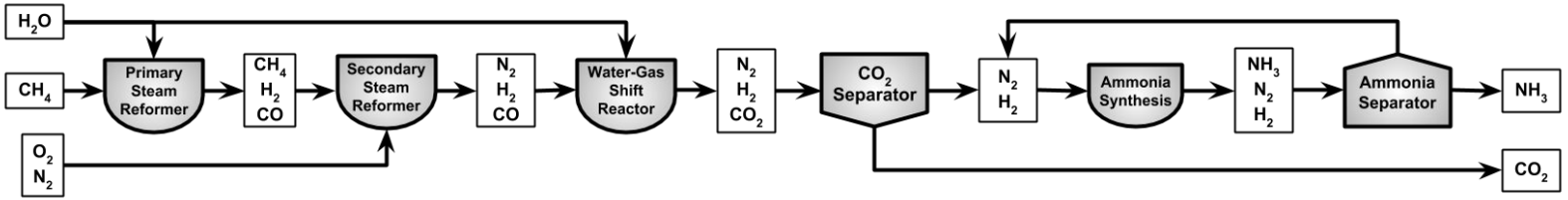
- Electrochemical PRR is extremely efficient
  - Near 100% atom and energetic efficiencies
- Milder than incumbent process (1500 °C)
- Potential to be zero-carbon (anodic OER)



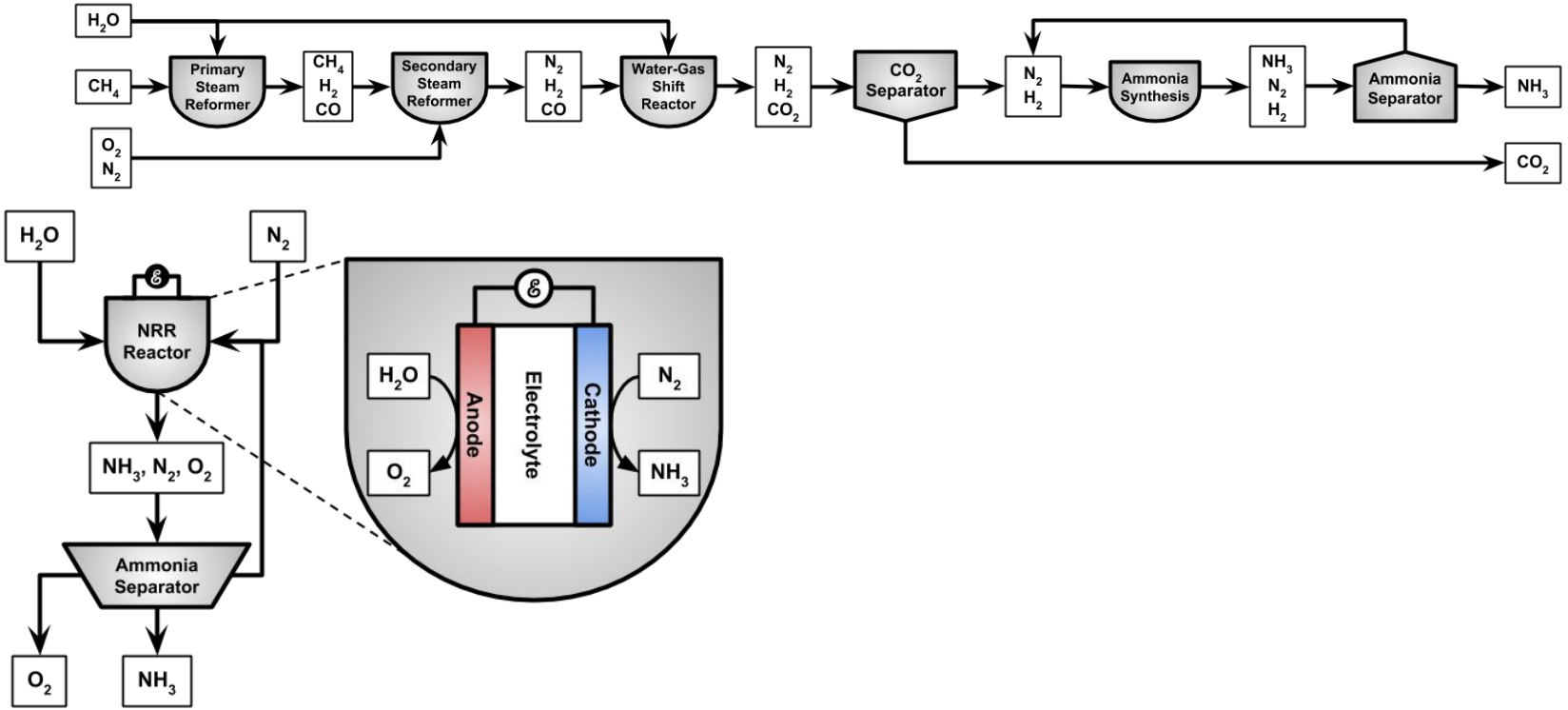
Electrochemical Nitrogen Reduction

routes to clean fertilizer synthesis

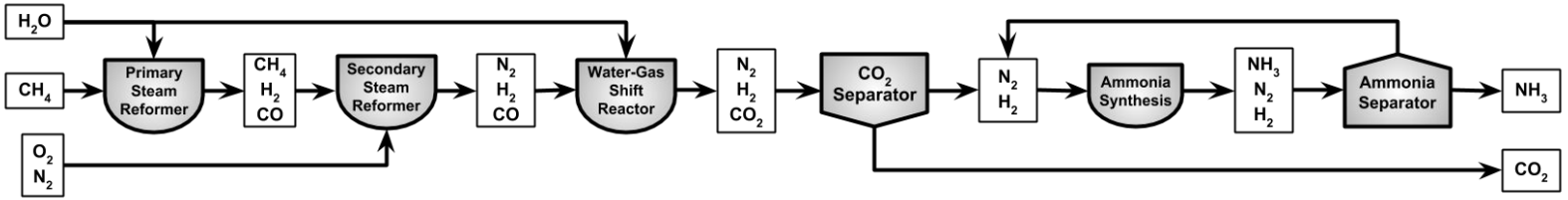
High-Pressure N_2 Electroreduction

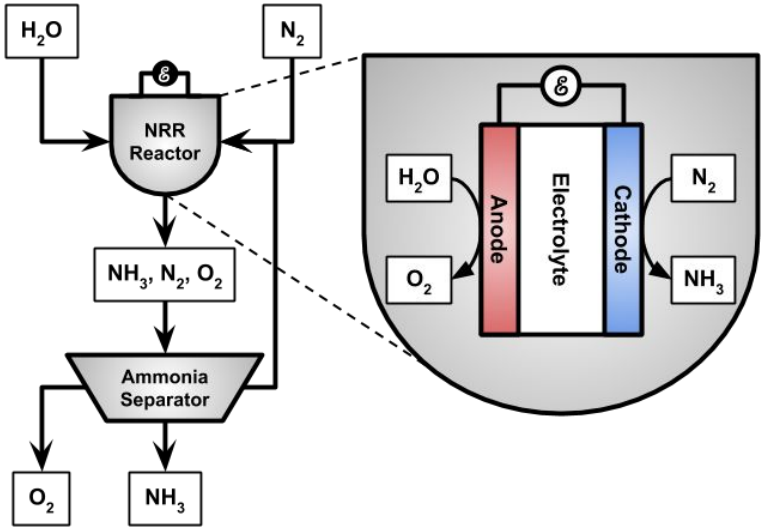


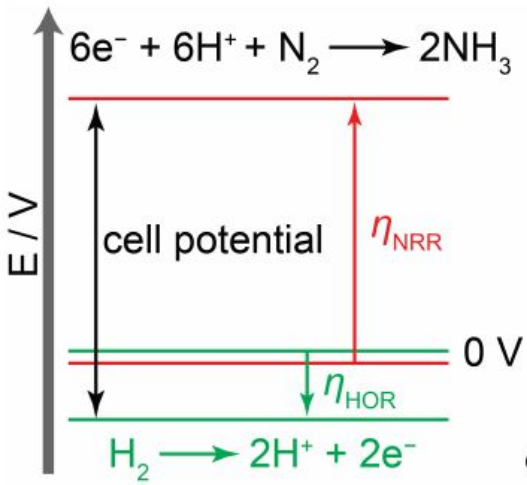
High-Pressure N_2 Electroreduction

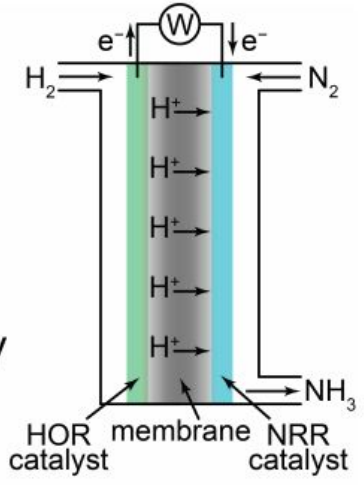


High-Pressure N_2 Electroreduction

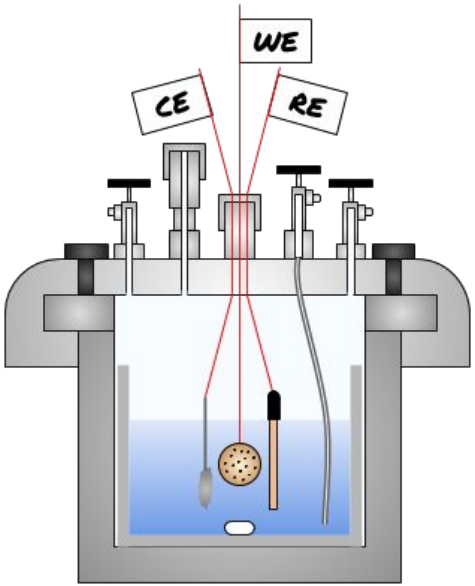








Custom High-Pressure NRR Setup



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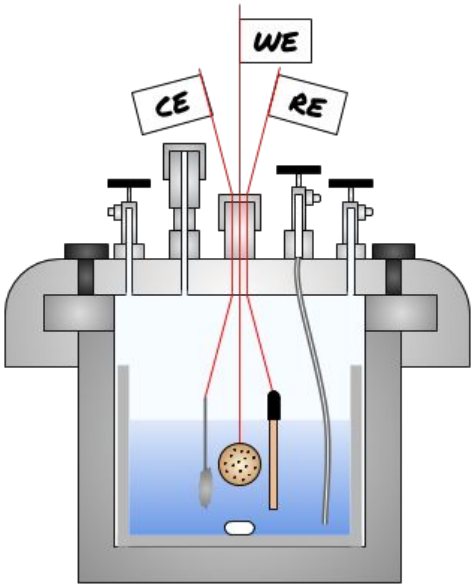
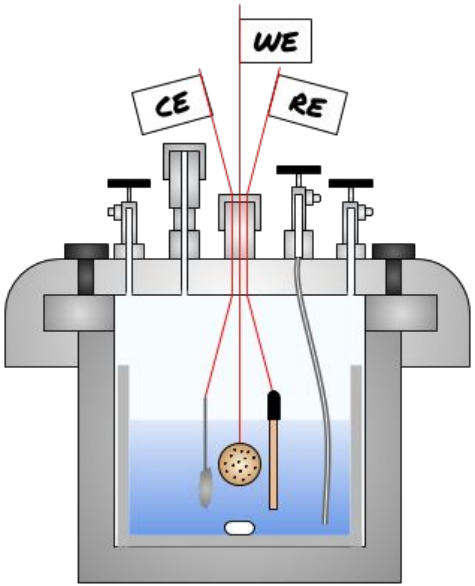


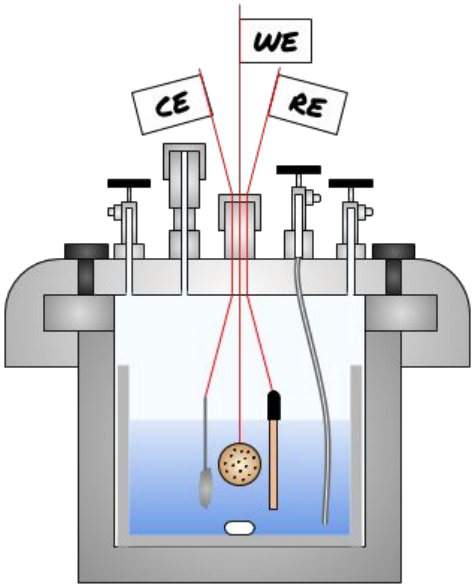
Custom High-Pressure NRR Setup

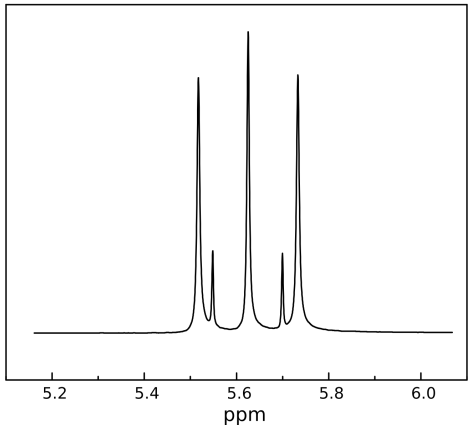
Quantify by colorimetry



Custom High-Pressure NRR Setup

Quantify by colorimetry and NMR





Copper Nitride is Active for NRR

Peak FE: 14% (1.67×10^{-5} mol m^{-2} s^{-1})

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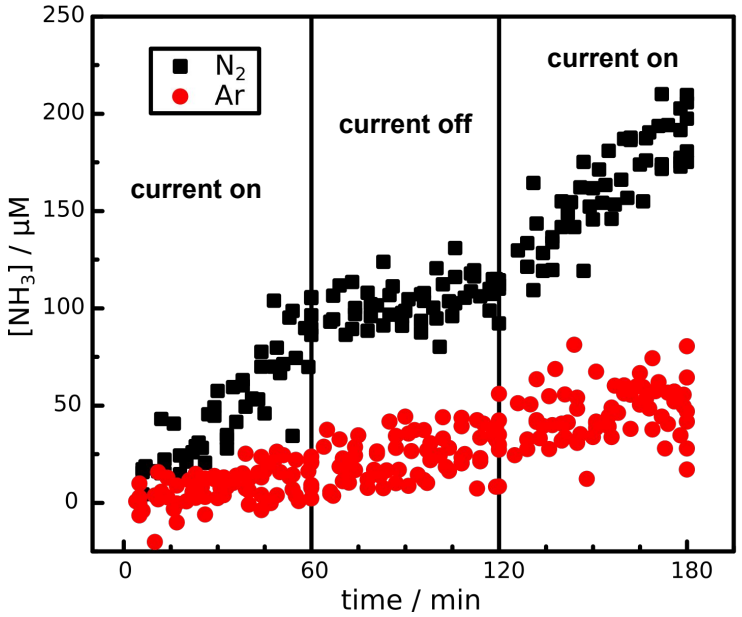

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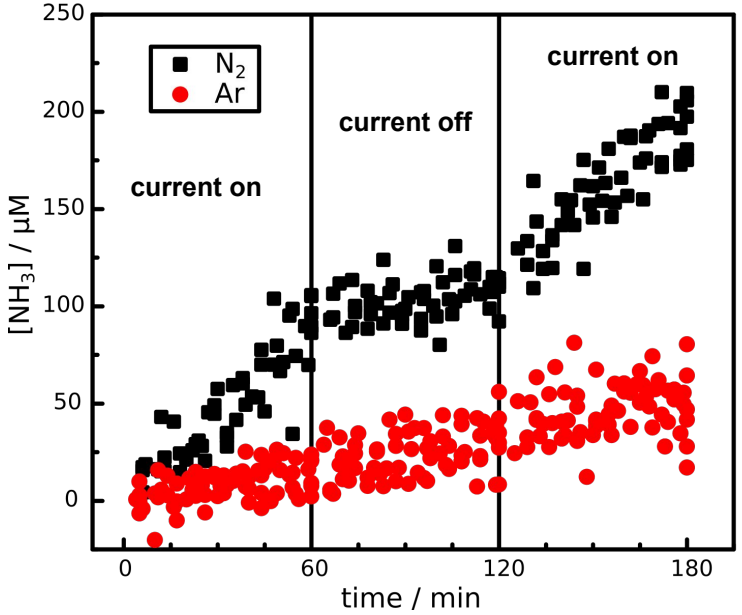
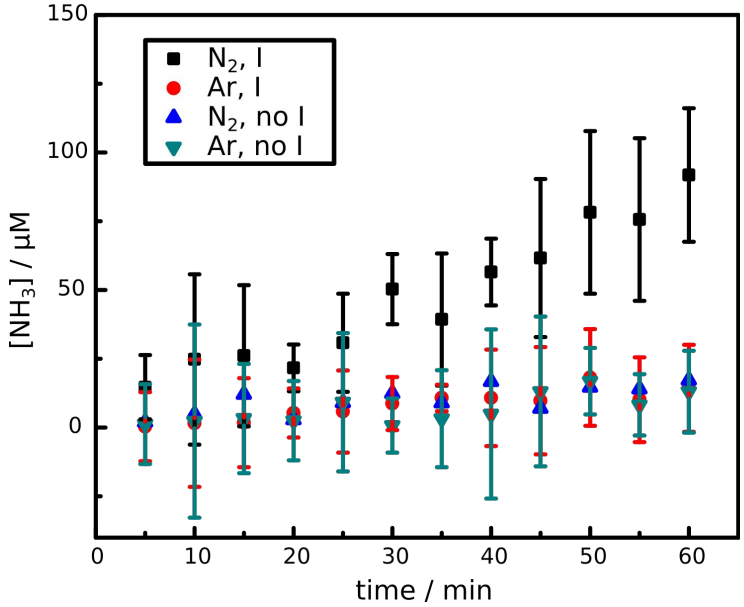
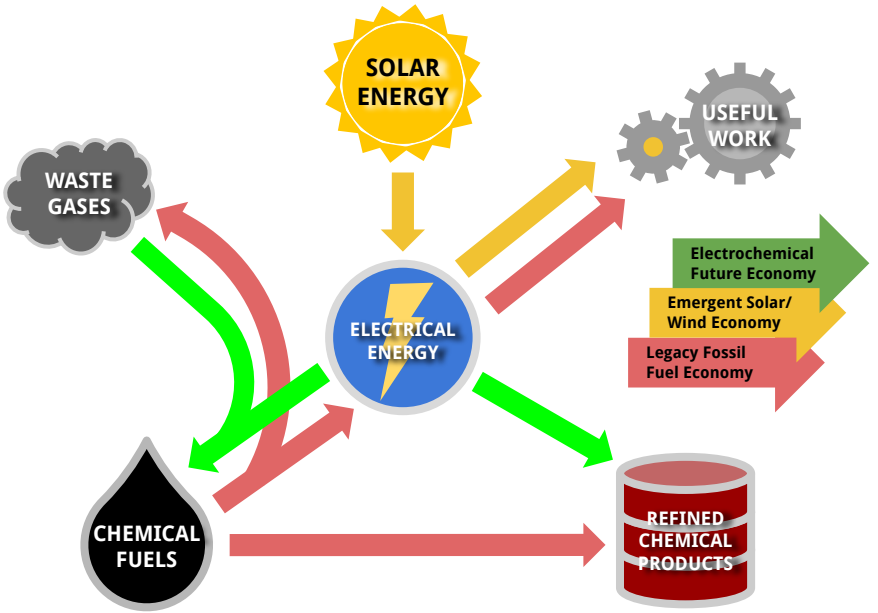


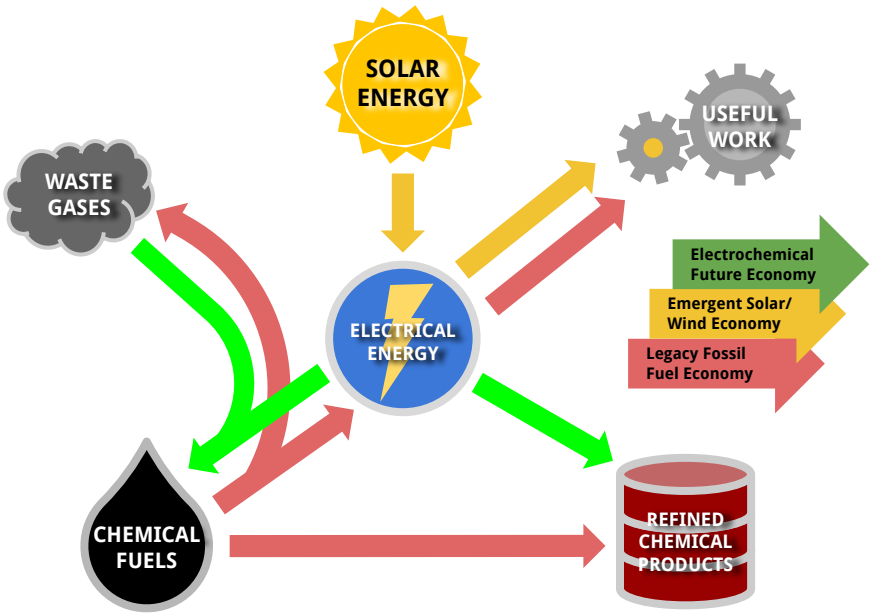


Conclusions & Outlook



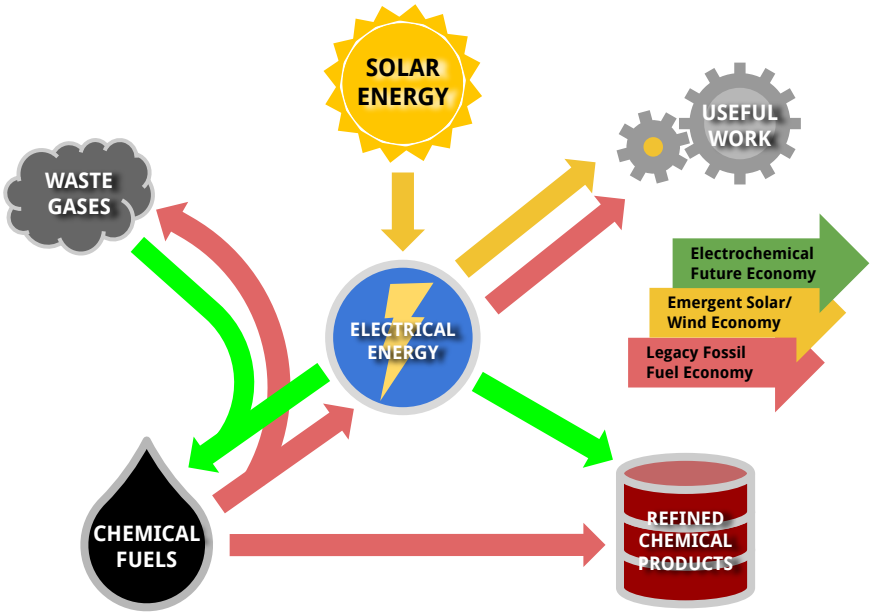
Conclusions & Outlook

- Applied pressure is a powerful handle for modulating NRR



Conclusions & Outlook

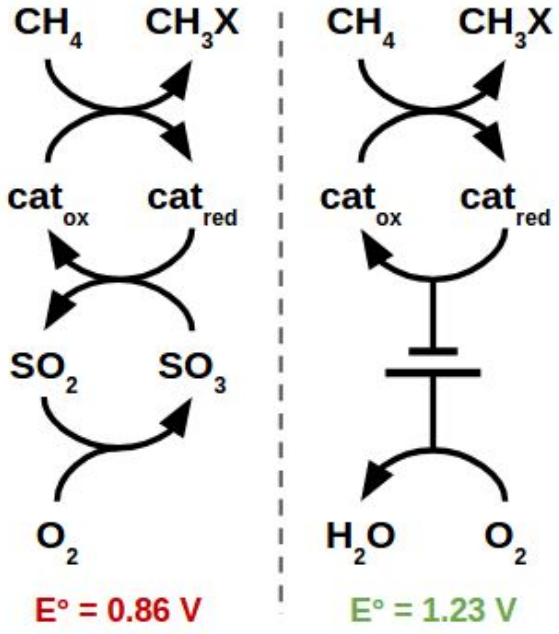
- Applied pressure is a powerful handle for modulating NRR
- Much work needed to achieve industrial viability



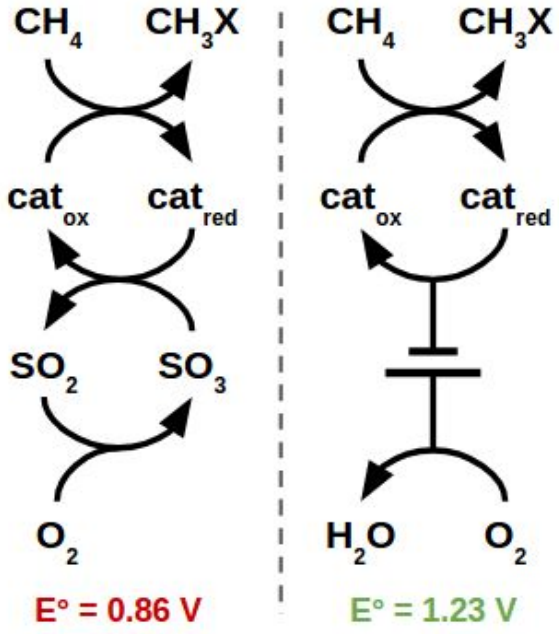
Methane Gas-to-Liquid Functionalization

scalable valorization of flared methane

Functionalized Methane Product Protection



Functionalized Methane Product Protection



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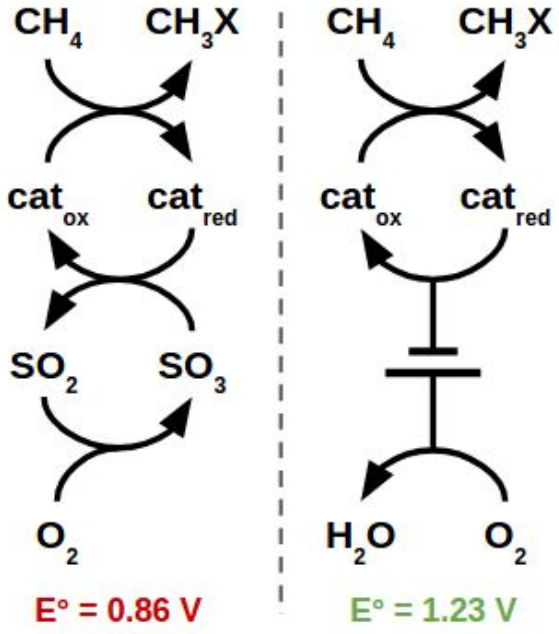
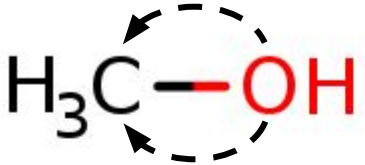
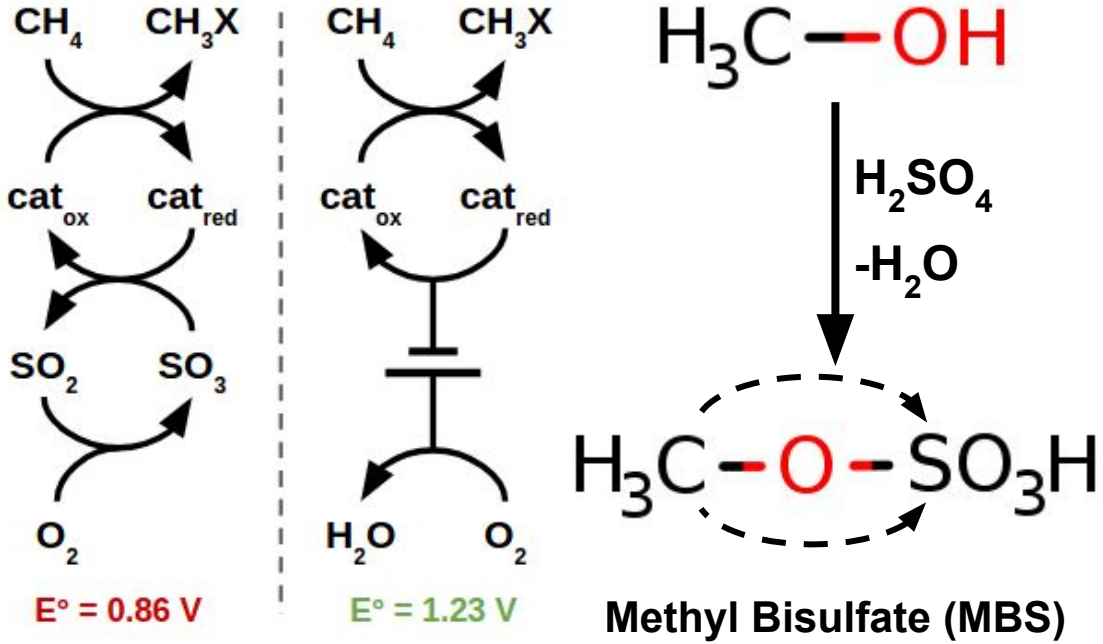


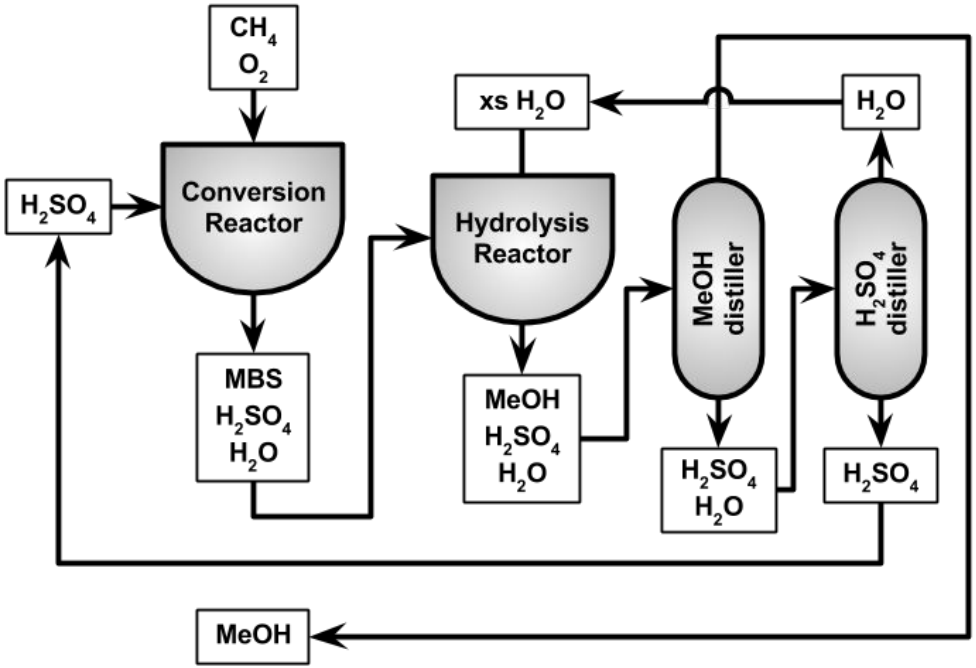


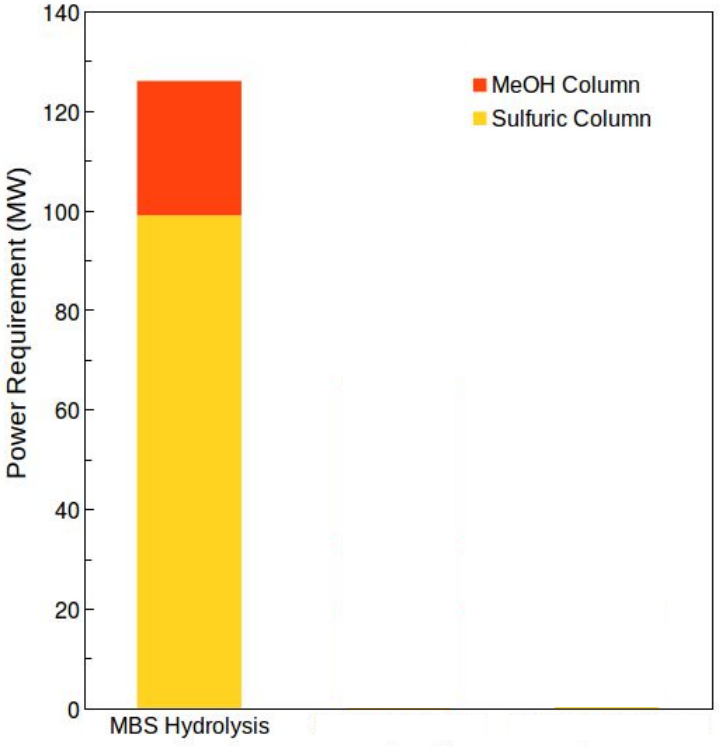
Functionalized Methane Product Protection

- MeOH → MBS esterification prevents overoxidation to CO_2



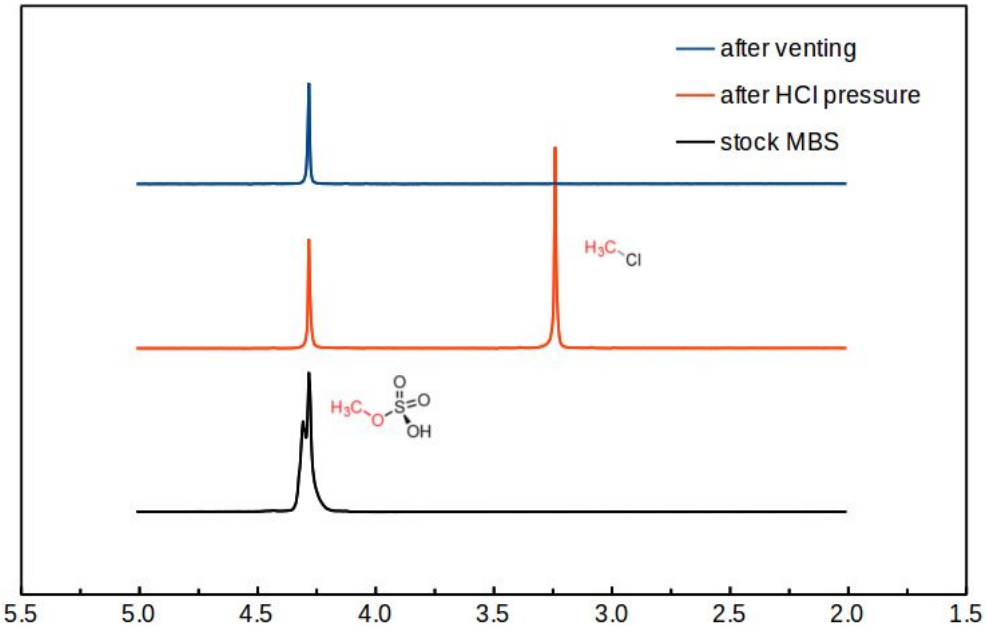
Industrial MBS Hydrolysis: Infeasible





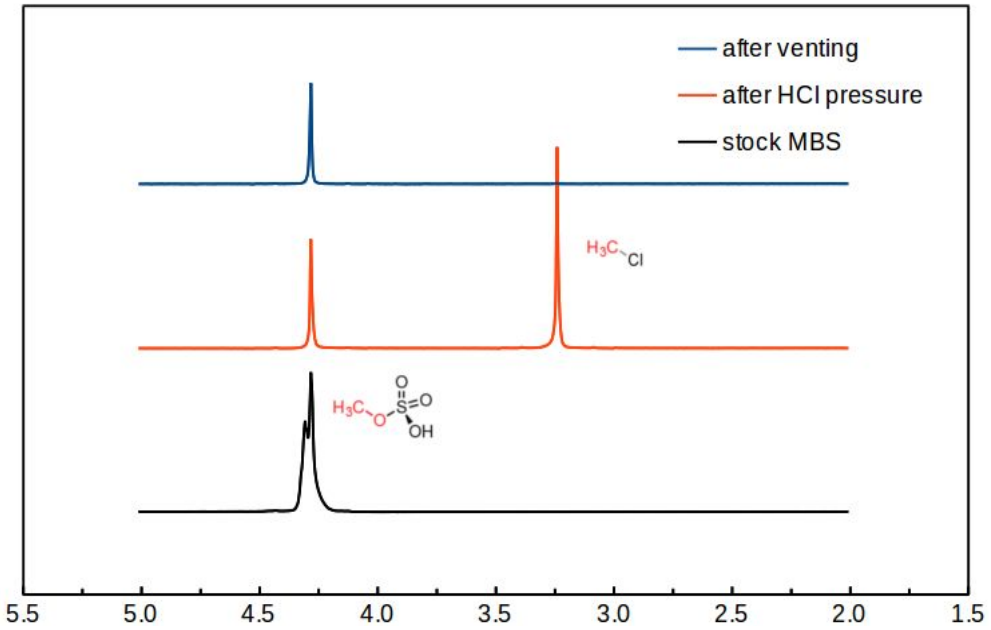
MeCl for MBS Product Separation

- Bottom to top:



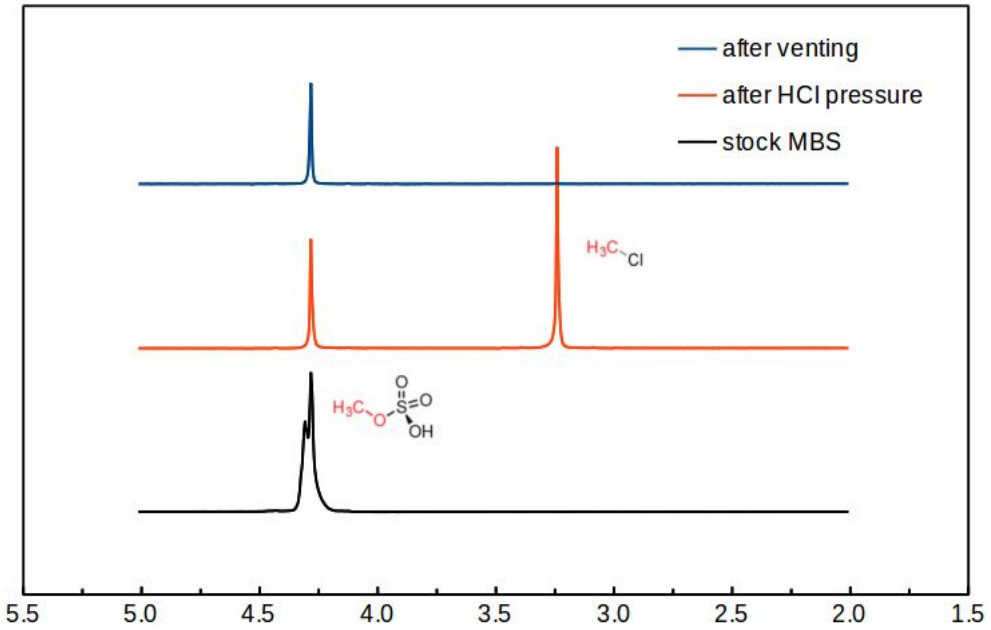
MeCl for MBS Product Separation

- Bottom to top:
  - Esterified MeOH in H_2SO_4
    - MBS + DMS



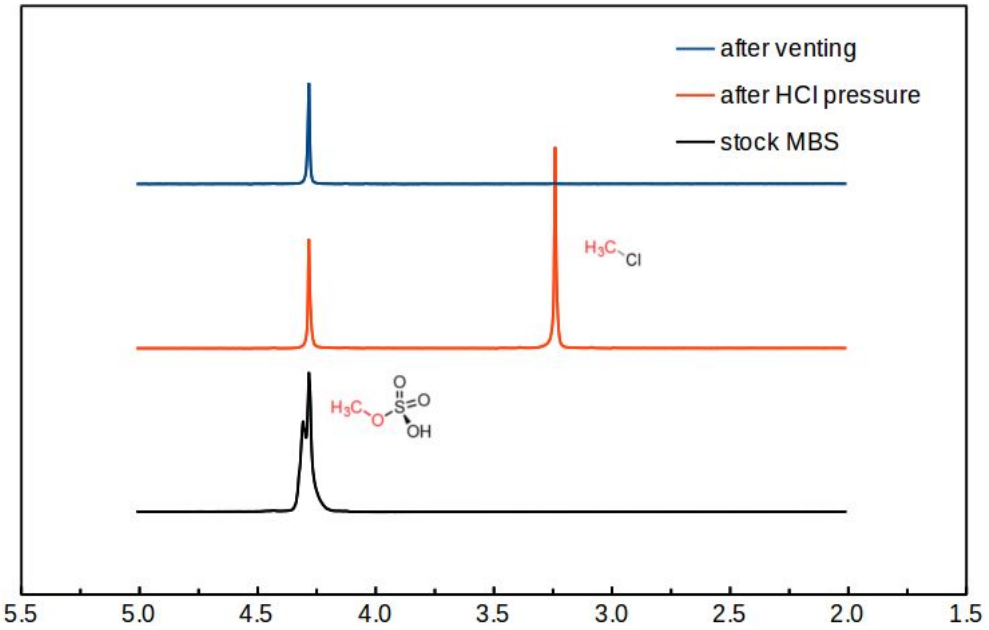
MeCl for MBS Product Separation

- Bottom to top:
  - Esterified MeOH in H_2SO_4
    - MBS + DMS
  - Pressurize with 150 psig HCl
    - Forms MeCl

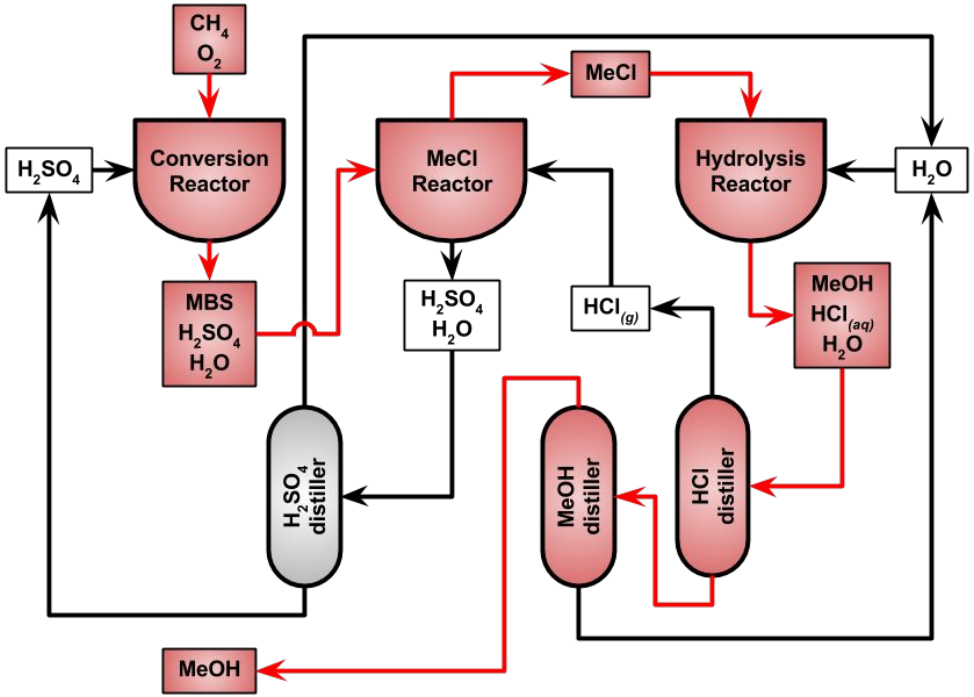


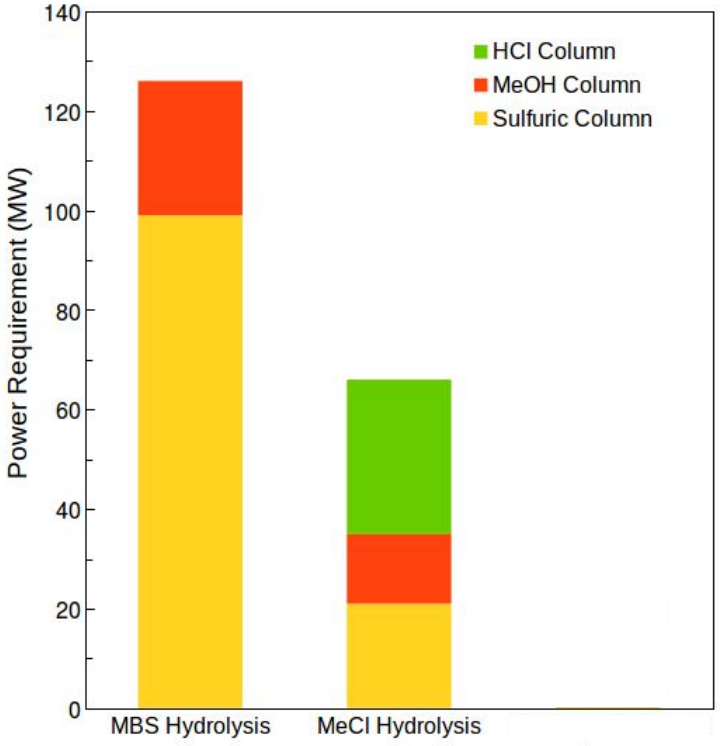
MeCl for MBS Product Separation

- Bottom to top:
  - Esterified MeOH in H_2SO_4
    - MBS + DMS
  - Pressurize with 150 psig HCl
    - Forms MeCl
  - Heat at 200C for 90 min
    - MeCl volatilizes

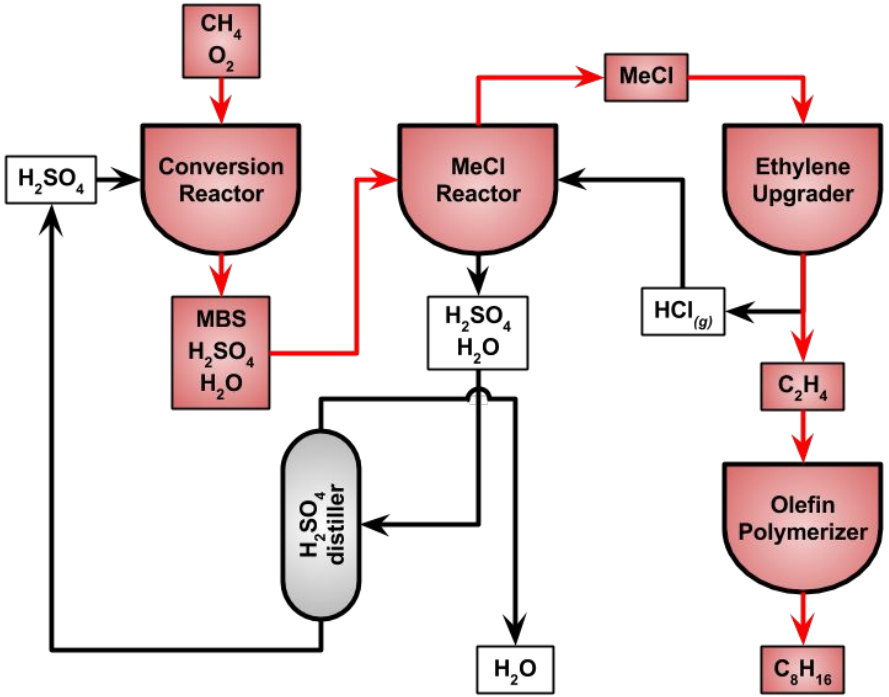


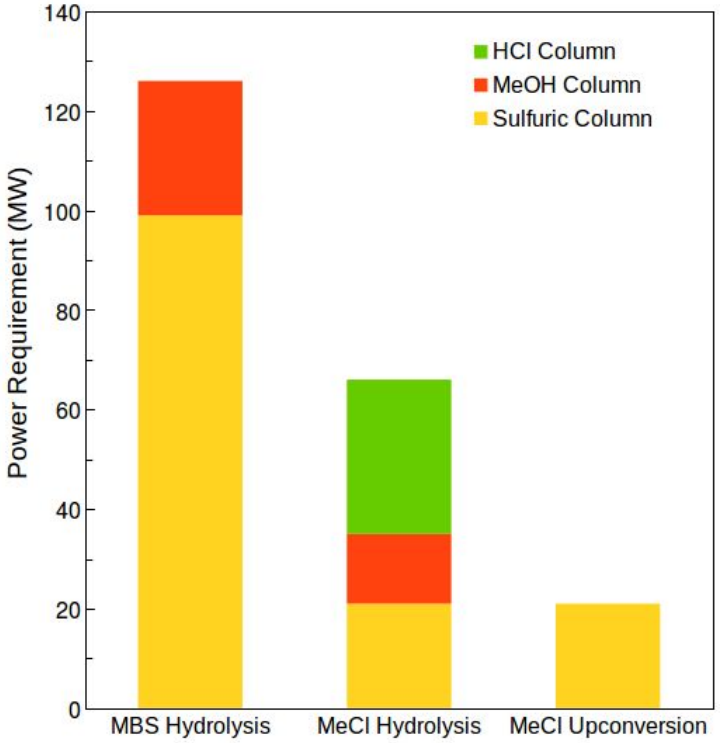
MeCl Hydrolysis: Reduced Distillation



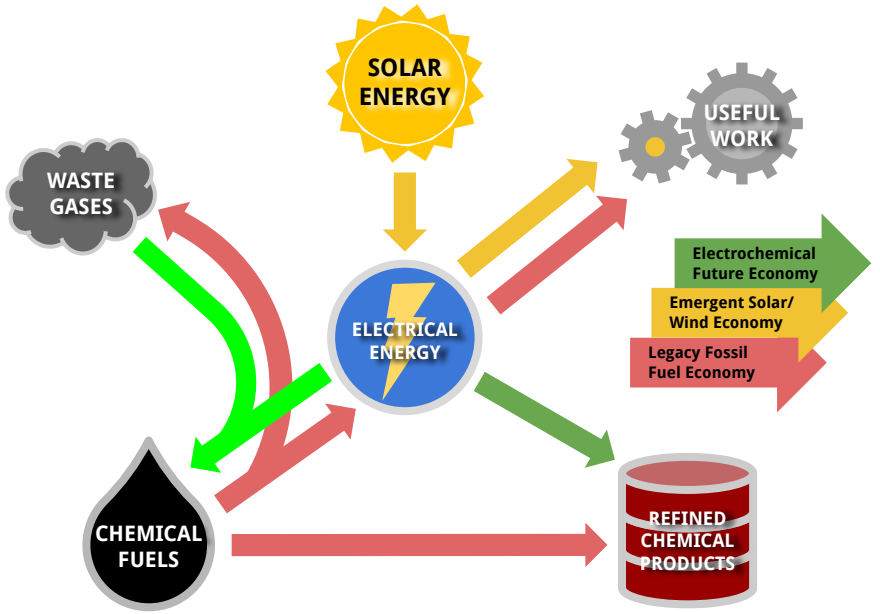


MeCl Upgrading: Industrially Viable



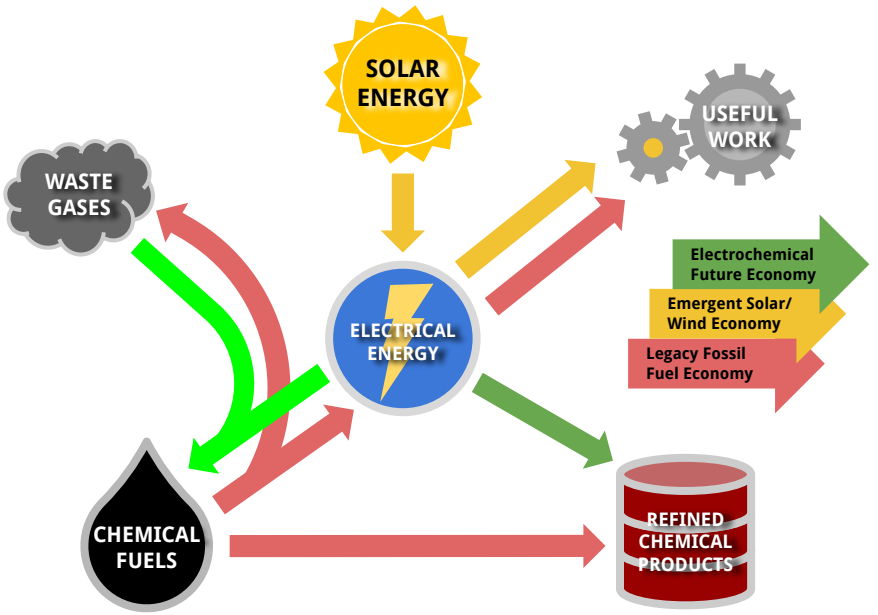


Conclusions & Outlook



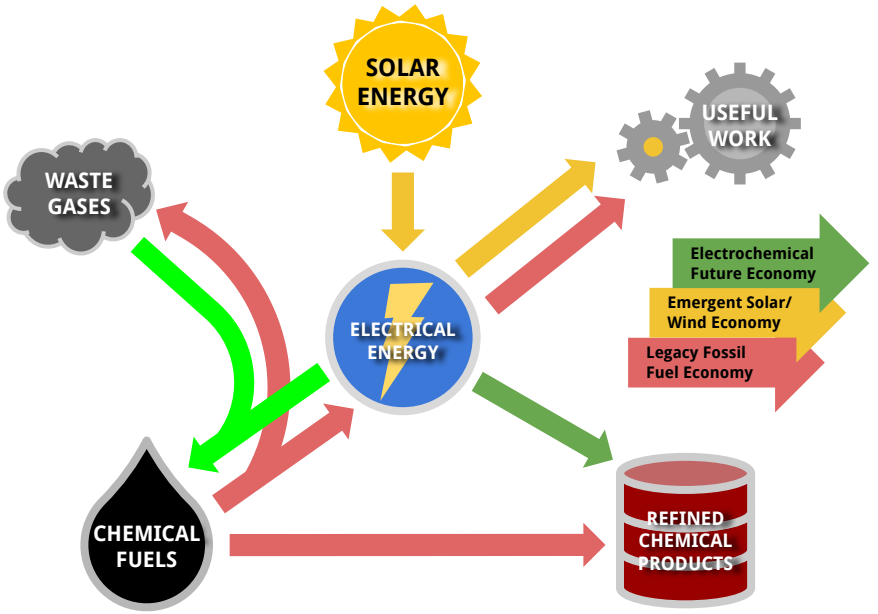
Conclusions & Outlook

- Efficiency is no guarantee of industrial viability



Conclusions & Outlook

- Efficiency is no guarantee of industrial viability
- Product separation can be as crucial as product generation



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Mohammed VI Polytechnic University