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Nanometer-Thick Cobalt-Iron Spinel Oxide Films for High Temperature Splitting of H_2O and CO_2

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Outline

- **Sandia "Solar To Petrol" program**

- **$Co_xFeO_{3-x}O_4$ ALD films on high surface area zirconia supports**
  - Thermochemical water splitting

Sandia Grand Challenge “Solar To Petrol” Program

The US Transportation Sector Consumes A Great Deal Of Petroleum

Every day the U.S. consumes ~20.7 million barrels of petroleum (2006) (that's ~10K gallons per second)

8.5 Billion Vehicle Miles/Day

>95% dependent on Petroleum

All Substitutes face significant risks, barriers, and uncertainties: one or more from technical, economic, societal, political, regulatory

Solve the Problem – we have been picking and then solving partial Solutions at best

58% is imported

Over 2/3 (68.3%) of the petroleum consumed in the US is used for transportation

84.1% Highway; 65.2% Light Duty

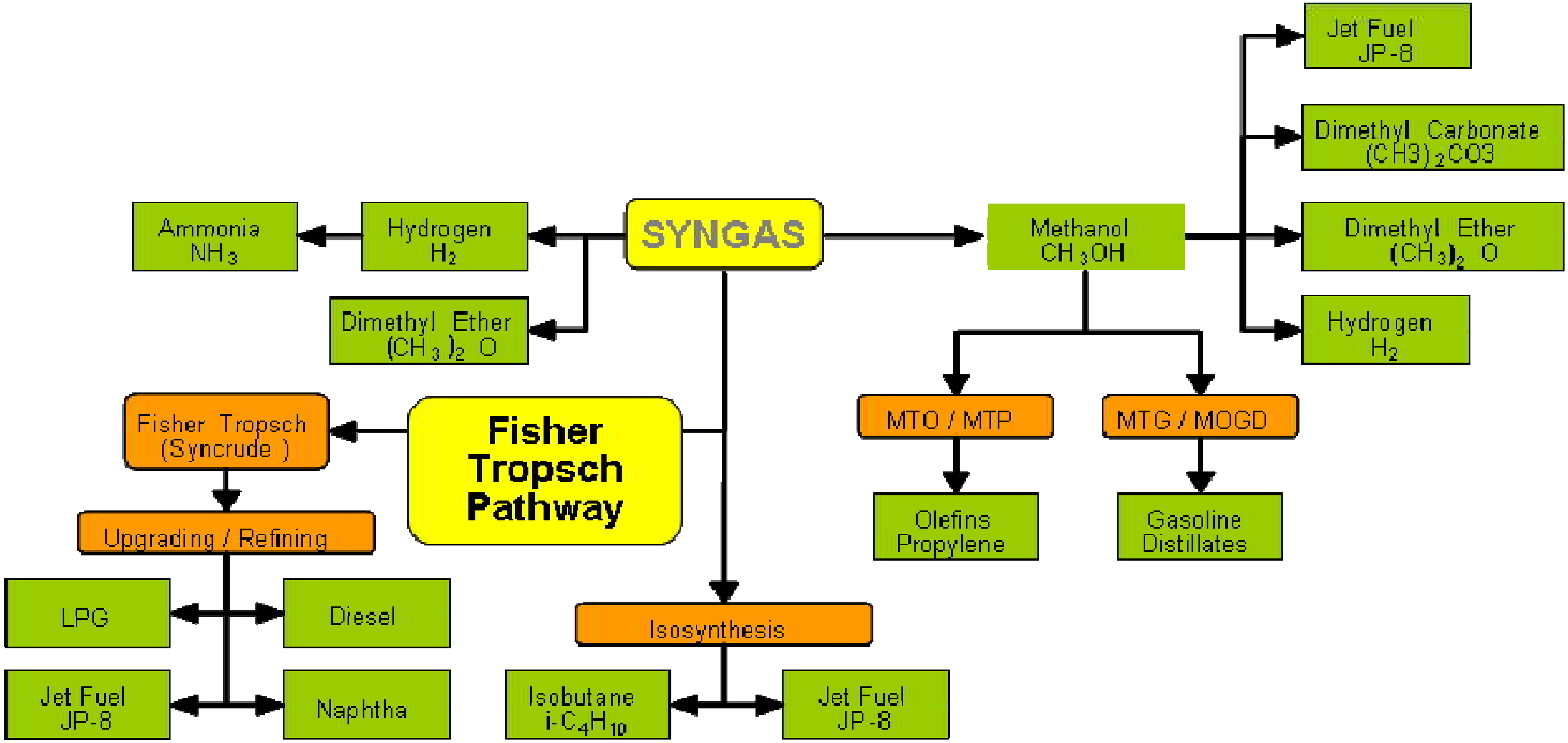
243M vehicles on the road in the US:

Median age ~8 yrs; cars ~9 yrs

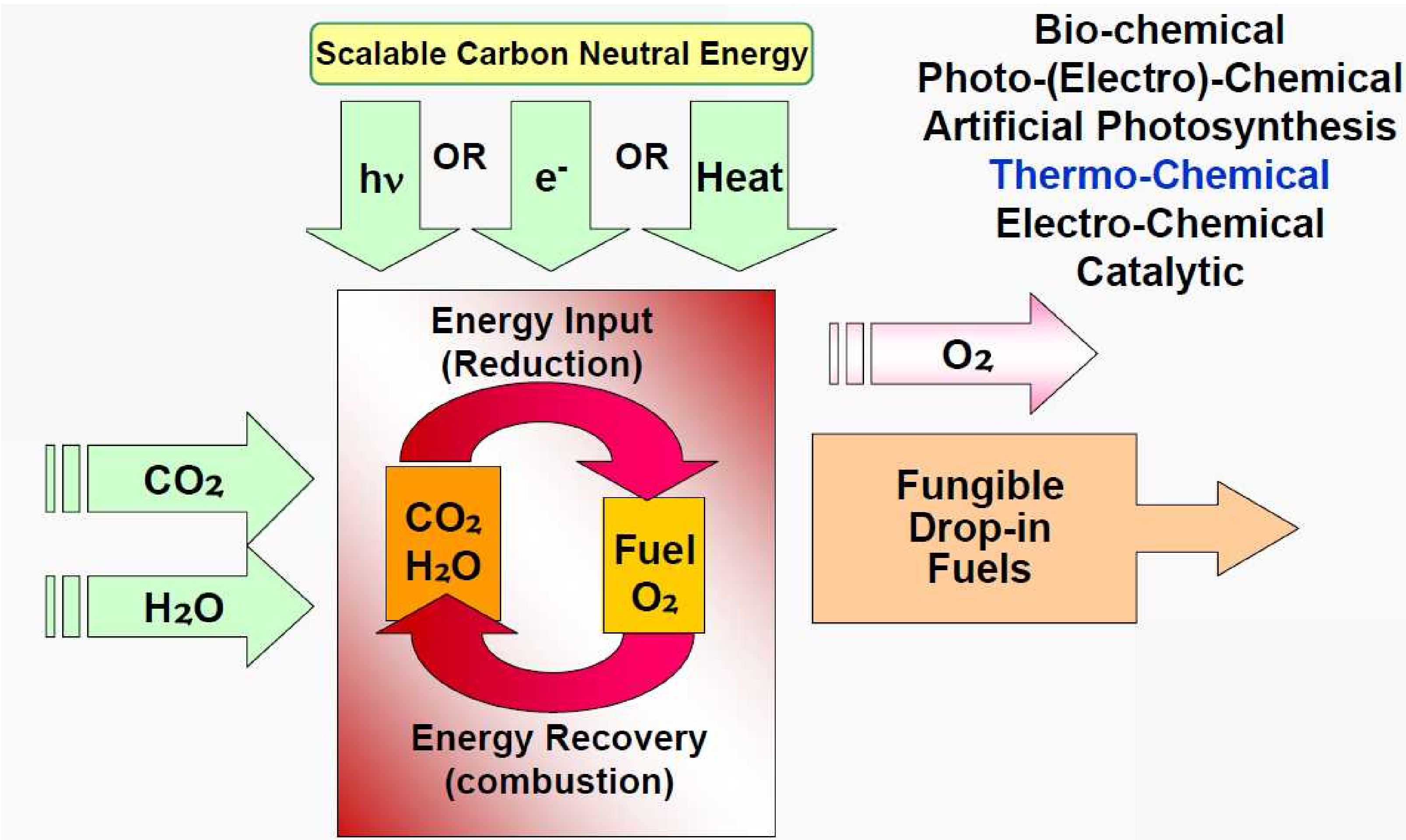
Median Lifetime of 1990 vehicles is ~17yrs

*Transportation Energy Data Book, Edition 27-2008

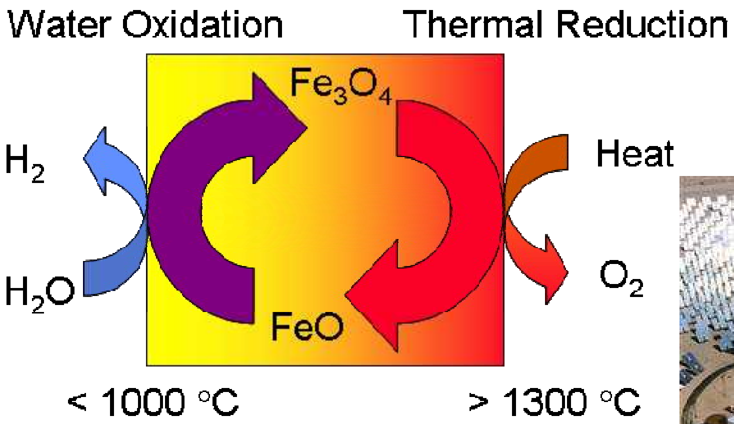
There Are Known Pathways To Synthesize Liquid Fuels From Synthesis Gas

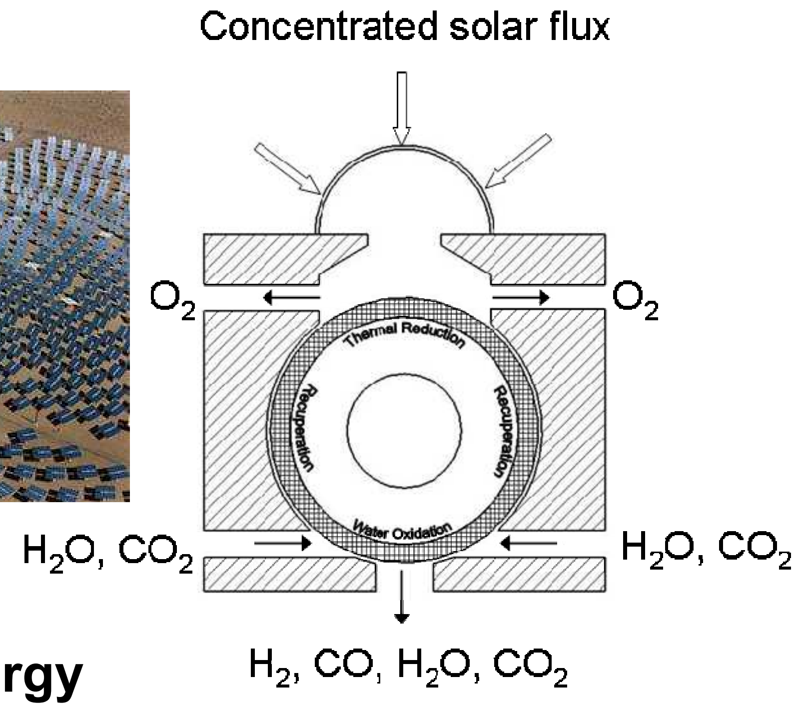


Carbon-Neutral Means To Produce Synthesis Gas Are Needed To Impact Global CO_2



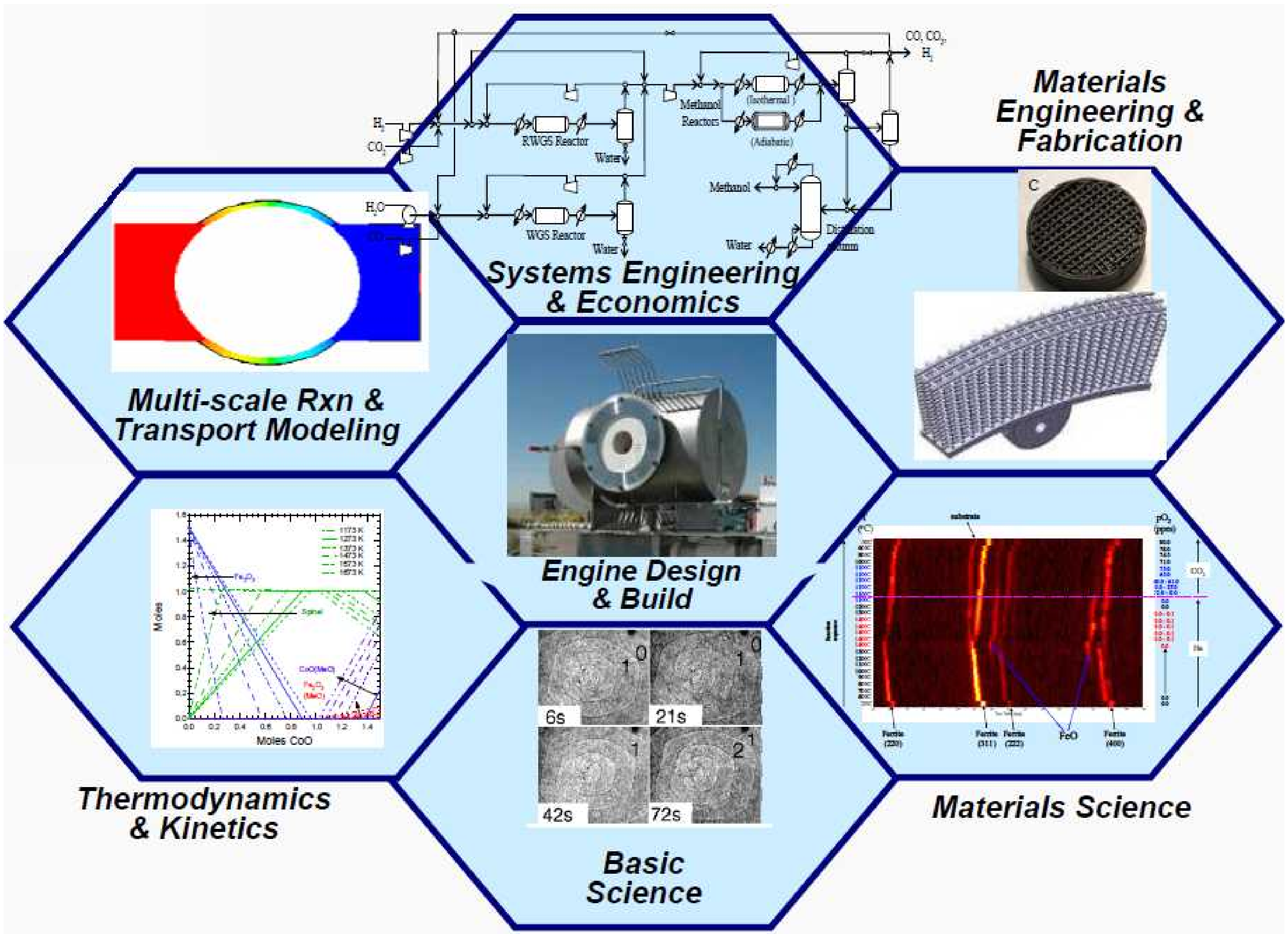
Vision Is To Recycle CO_2 and H_2O into Fuel Using Concentrated Solar Power





- **Power Towers concentrate solar energy**
  - Thousands of suns
- **Continuous process**
  - Fe($^{+2}$) in FeO to Fe($^{+3}$) in Fe_3O_4
  - Rotating ring design for efficient heat recovery

Sandia's Large Scale Multi-Disciplinary Effort To Create A High Thermal Efficiency Prototype



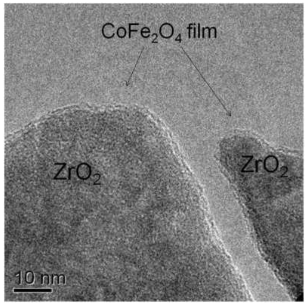
$Co_xFeO_{3-x}O_4$ ALD films on high surface area zirconia supports

Materials Are The Key To Success For Solar Energy Storage Program

- **Open structures necessary for good light penetration**
  - Radiative transport more important than conduction
- **Cycle-to-cycle stability and durability**
  - 1 to 2 minute redox cycles
    - 1723 K to < 1473 K
  - Remain chemically active
  - Maintain mechanical integrity
    - Limit sintering, spalling, fracture
- **High surface areas desired**
  - Process efficiency dependent on extent of conversion

engineered shapes

coated particles

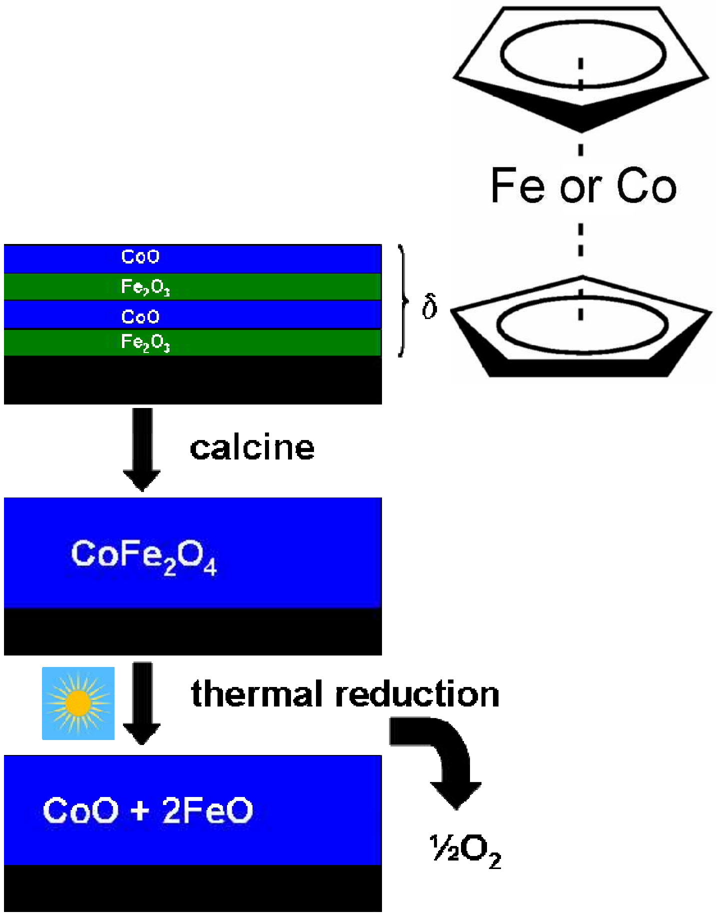


Investigate The Use Of Thin Film Cobalt Ferrite Spinel

- **Precisely engineered platform**
  - Composition
  - Microstructure
  - Thickness
- **Atomic Layer Deposition**
  - Conformal coverage of arbitrary shapes
    - High surface-area supports
  - Precise control of thickness and stoichiometry
  - Nano-scale film thicknesses
    - Mitigate bulk diffusion limitations of fully dense parts
    - Best use of solar flux (only heat active material)

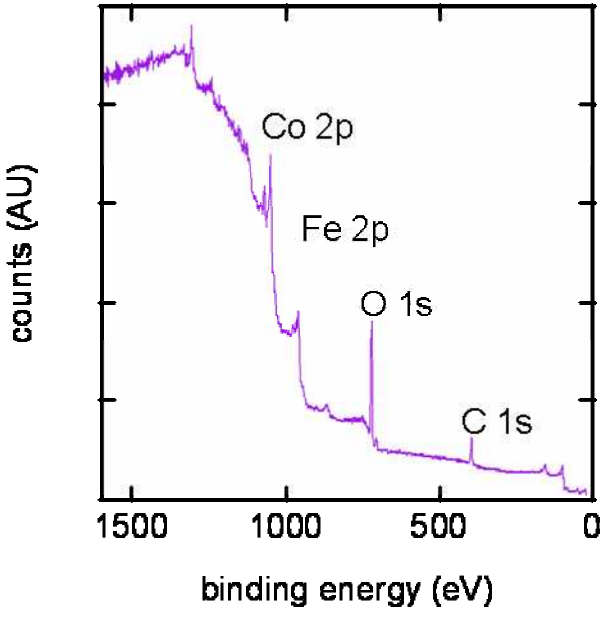
ALD Method

- **Self-limiting deposition chemistry**
  - Successive cycles of cobaltocene and ferrocene oxidation @ 640-800 K
  - Calcine @ 1650 K, reduce @ 1723 K
- **Number of deposition cycles for each element determines film stoichiometry**
  - 15 Å per cycle
- **Range of materials prepared**
  - Fe_3O_4, $Co_xFe_{3-x}O_4$ (0.6 < x < 1.5)
  - Single crystal YSZ and sapphire flats
  - ZrO_2 nano-particles
  - High surface area nano-porous YSZ supports
  - Various mass loads and film thickness



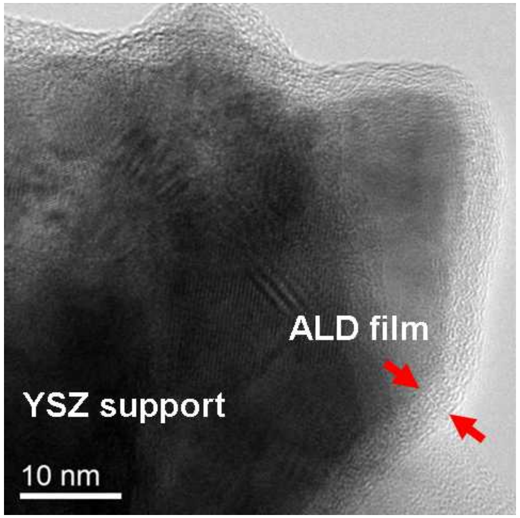
Scheffe, J. et al. *Thin Solid Films* **517**, 1874 (2009)

XPS, Surface Raman, And TEM Analysis Confirms Quality Of “As Deposited” Films

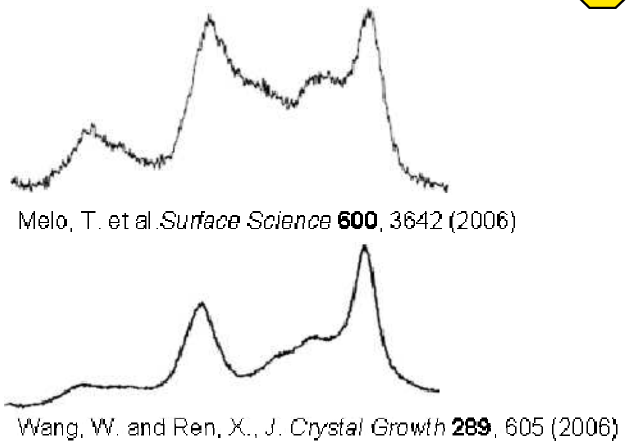


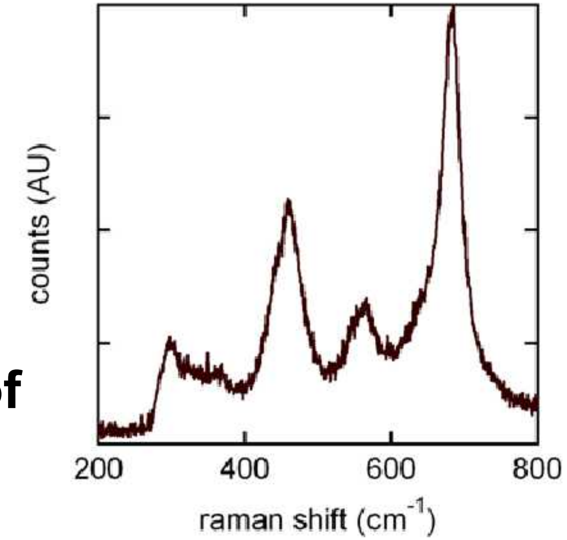
- **No surface Zr or Y evident in XPS**

- **Uniform film thickness**

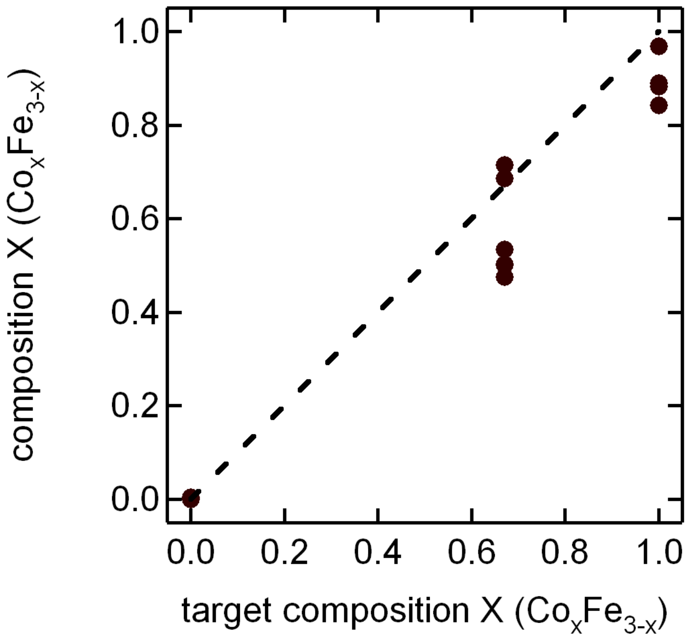


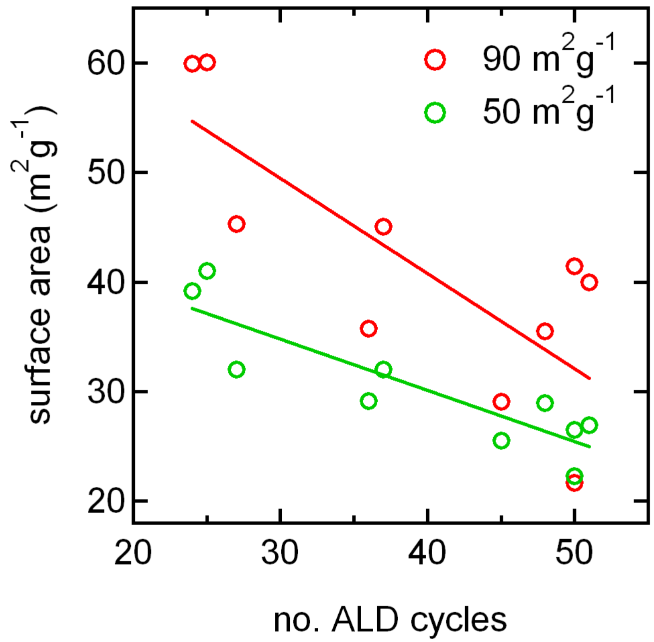
- **Raman spectra of $CoFe_2O_4$**





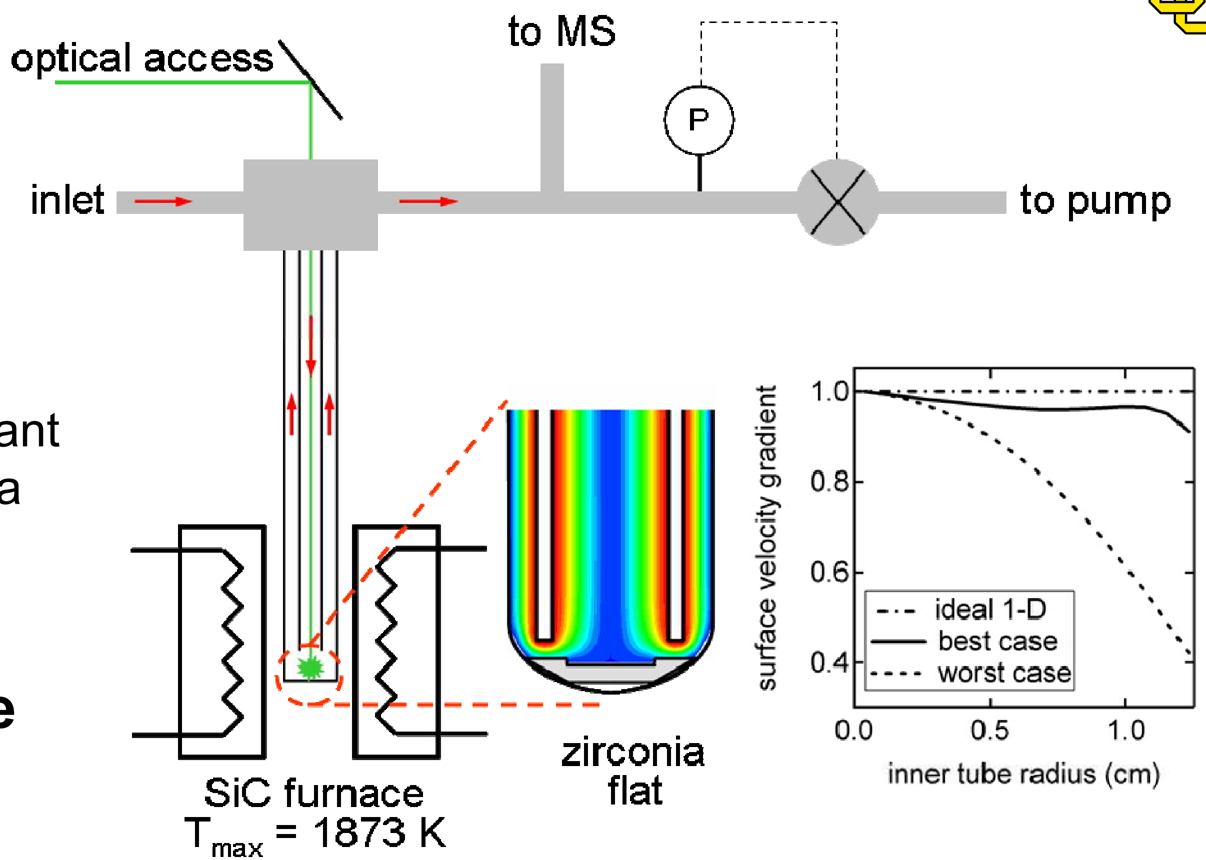
ICP And BET Analysis Confirms Film Composition And Active Area





- **Able to achieve target composition on high surface area YSZ supports**
  - 25 to 50 cycles depending on film thickness and mass loading
- **Reduced surface area likely due to clogging of pores**

Redox Behavior Characterized In An Idealized Stagnation Flow Reactor (SFR)

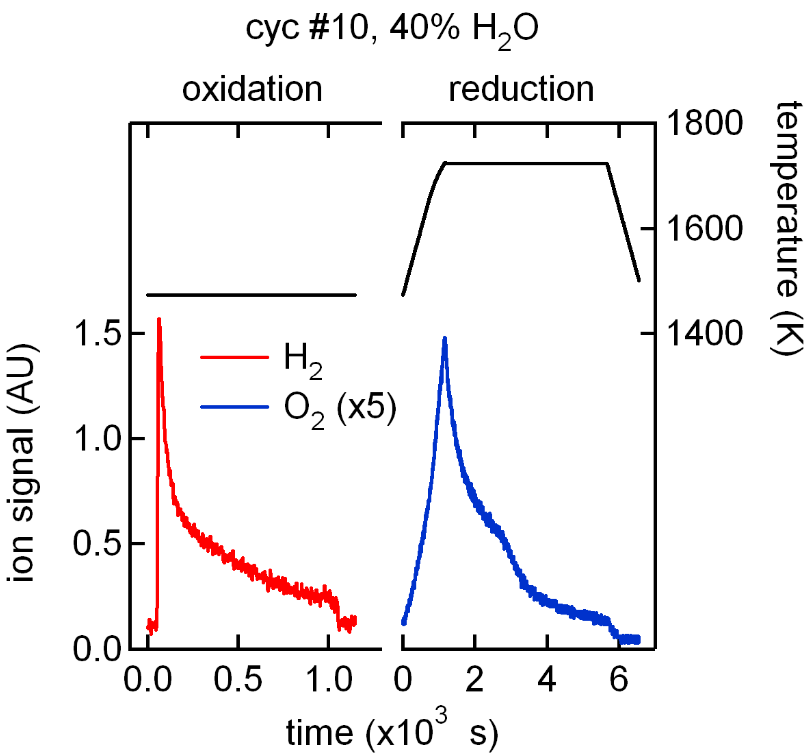


- **Computer-aided design of SFR**
  - 1-D flow field important for model-based data reduction
- **Modulated effusive source MS**
  - High sensitivity

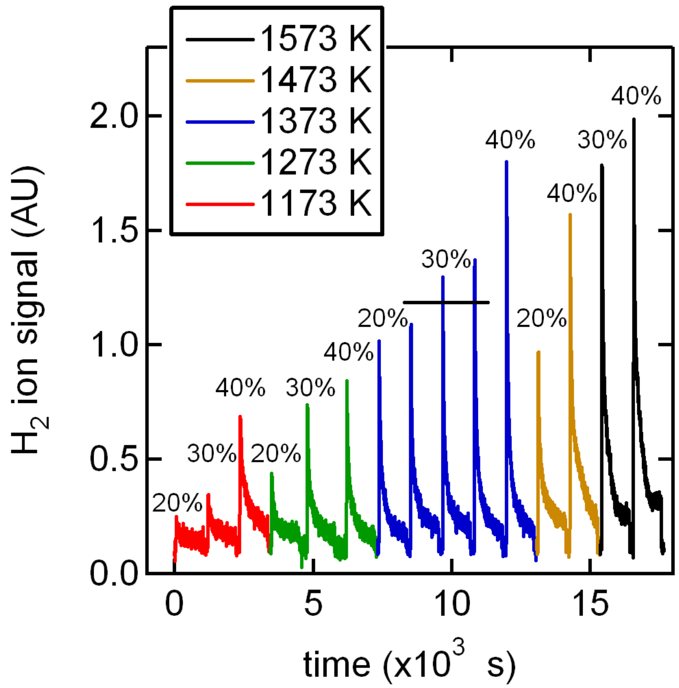
    5 ppm detection limits

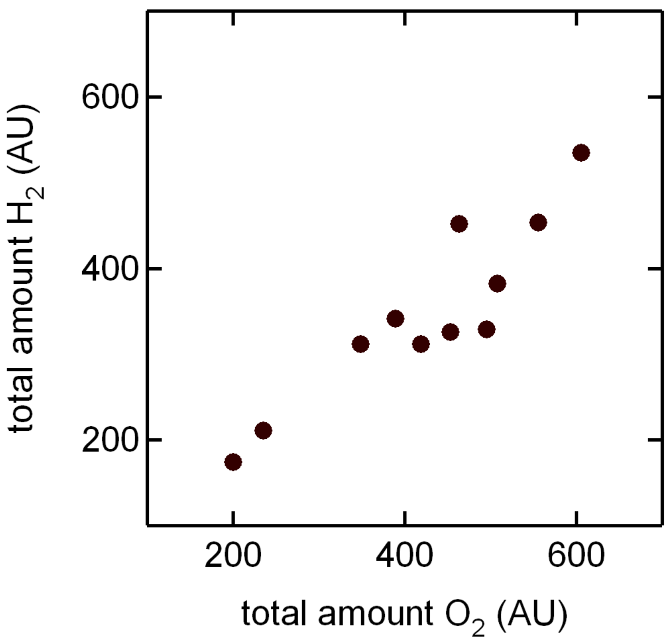
Oxidation And Reduction Of $Co_{0.9}Fe_{2.1}O_4$

- **H_2 production rate consistent with observations on powder and solid systems**
  - High peak rate that gradually tails to a plateau
  - Should this be true?
    - ALD films dominated by surface effects
- **Evidence to suggest the plateaus are a steady-state condition and do not go to zero**
  - Catalytic
    - WGS-like behavior?
  - Eventually may produce more H_2 than predicted by FeO content



ALD Films Remain Active For Many Redox Cycles

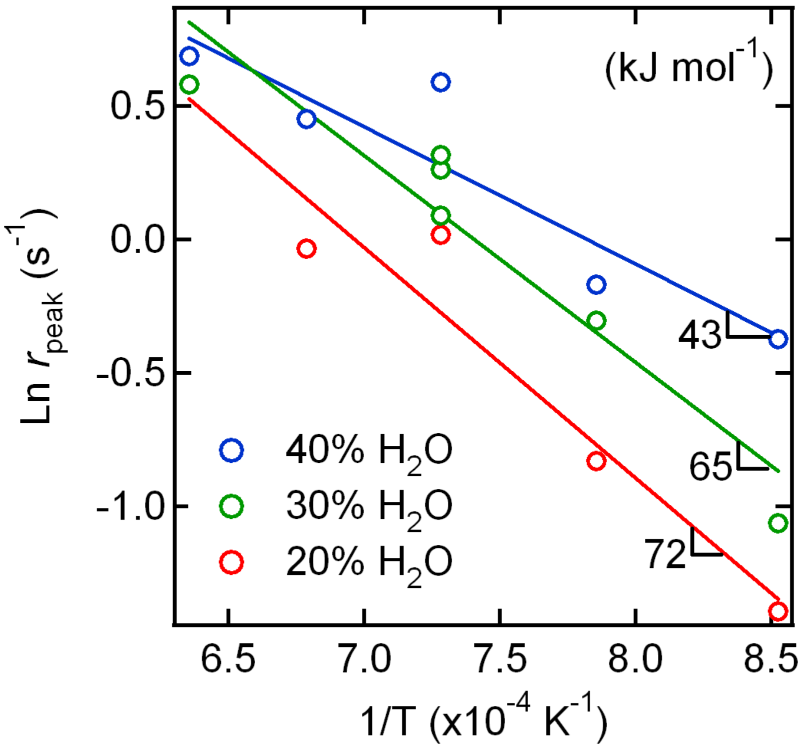




- **Dependence on H_2O pressure and temperature taken on a single sample (> 20 cycles)**
  - H_2O flow rate many orders of magnitude greater than H_2 production rate
- **H_2 production rate and O_2 evolution correlate well (so far)**
  - Plateaus may be a steady-state condition however material still stores O_2

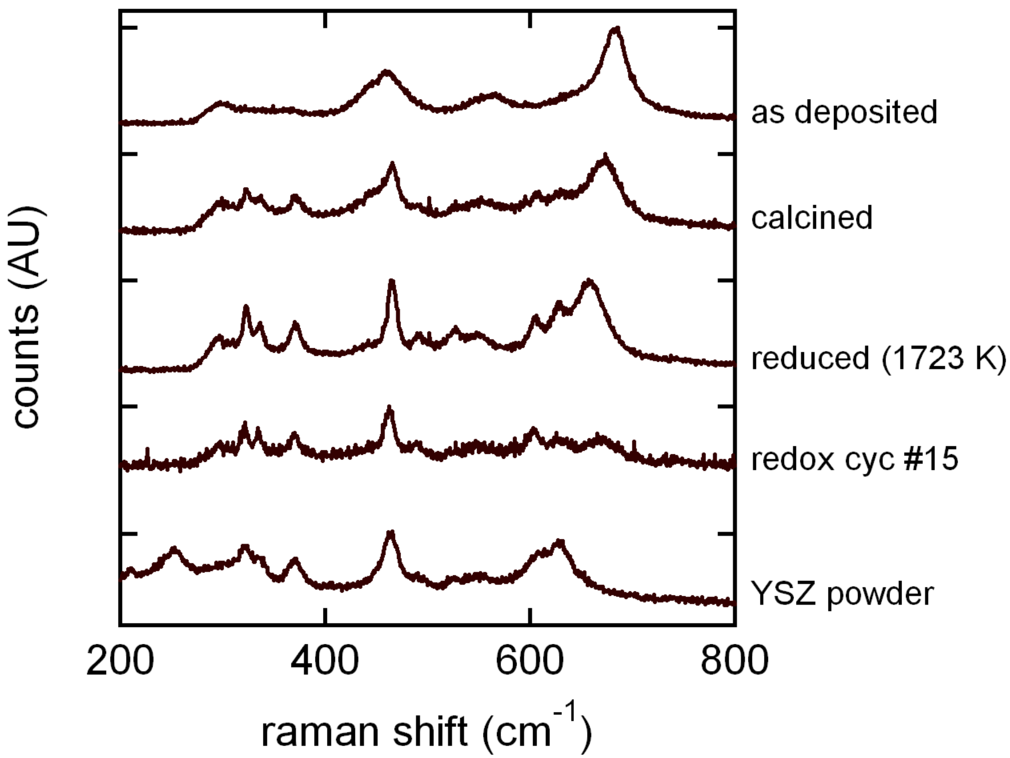
Activation Energy For Peak H_2 Production Rate May Not Support Fe Cation Diffusion Mechanism

- **E_a for Fe diffusion in FeO**
  - 100-150 kJ/mol
  - Still valid at high T?
- **E_a for Fe diffusion in Fe_3O_4**
  - > 200 kJ/mol
- **E_a for *peak* H_2O reduction agree with energetics of Fe-based WGS catalysts**
  - Low temperature ΔH_{ads} chemisorbed H_2O on (111) Fe_3O_4 ~ 65 kJ/mol



Raman Spectra Indicate That ALD Film Properties Change With Cycling

- **Spectral features of polycrystalline YSZ are present in cycled material**
  - Fe has limited solubility in stabilized zirconia
- **Still characterizing films with XPS and TEM**
- **Materials remain highly active up to 20 cycles**
  - Very consistent behavior



Concluding Remarks

- **ALD engineered ferrite films on nano-porous YSZ supports are viable materials for high temperature thermochemical water splitting applications**

- **Observed behavior representative of a complex water reduction mechanism**
  - Fast initial H_2 production rate followed by a slowly evolving "plateau"
  - Energetics may not support Fe cation diffusion as a rate limiting process for the peak rate
    - Still must resolve the E_a for the "plateau" behavior
  - Could be WGS-like behavior
    - Competition between thermal reduction and water oxidation

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