Liquid Fuel Processing Using Catalytic Membrane Reactors

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Outline

- **Conclusions Phase I; Goals Phase II**
- **Background**
  - Catalytic Membrane Reactors
  - Thermodynamic Considerations
  - Catalysts
- **Phase I Results**
- **Phase II Plans**

Level of Effort Phase I

- $100,000
- Nine months
- Screened ~40 catalyst formulations
- Used pump-grade diesel fuel ~200 ppmw S
- Preferred catalyst run 2 months

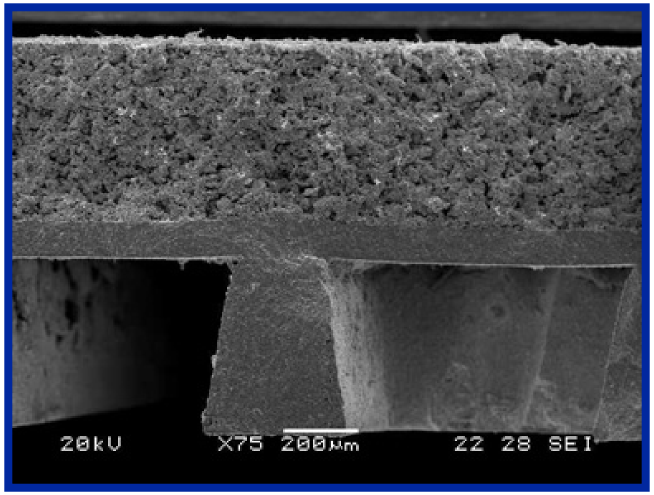
Goals – Phase II

Fabricate prototype catalytic membrane reactor for conversion of commercial grade diesel fuel into synthesis gas.

- **Eliminate deposition of carbon in cool zones of reactor by using self-cleaning reactor walls which diffuse/effuse oxygen.**
- **Minimize/eliminate use of noble metal catalysts.**
- **Minimize/eliminate nitrogen and recirculation of CO_2 and H_2O.**

Previous Work: Catalytic Membrane Reactors Using Oxygen Transport Membranes for Reforming of Natural Gas

- **Methane and steam streamed past porous layer**
- **Air streamed past slotted side**



Noble Metal Catalyzed Porous Layer

Dense Perovskite Layer

Slotted Air Side

- **Perovskite ceramic material: $La_{1-x}Ca_xFeO_{3-\delta}$**
- **Oxygen flux of 17 $mL \cdot min^{-1}\ cm^{-2}$ (STP).**
- **Methane reforming rate of 24 $mL \cdot min^{-1}$; hydrogen production >48 $mL \cdot min^{-1}$ (STP) per wafer.**

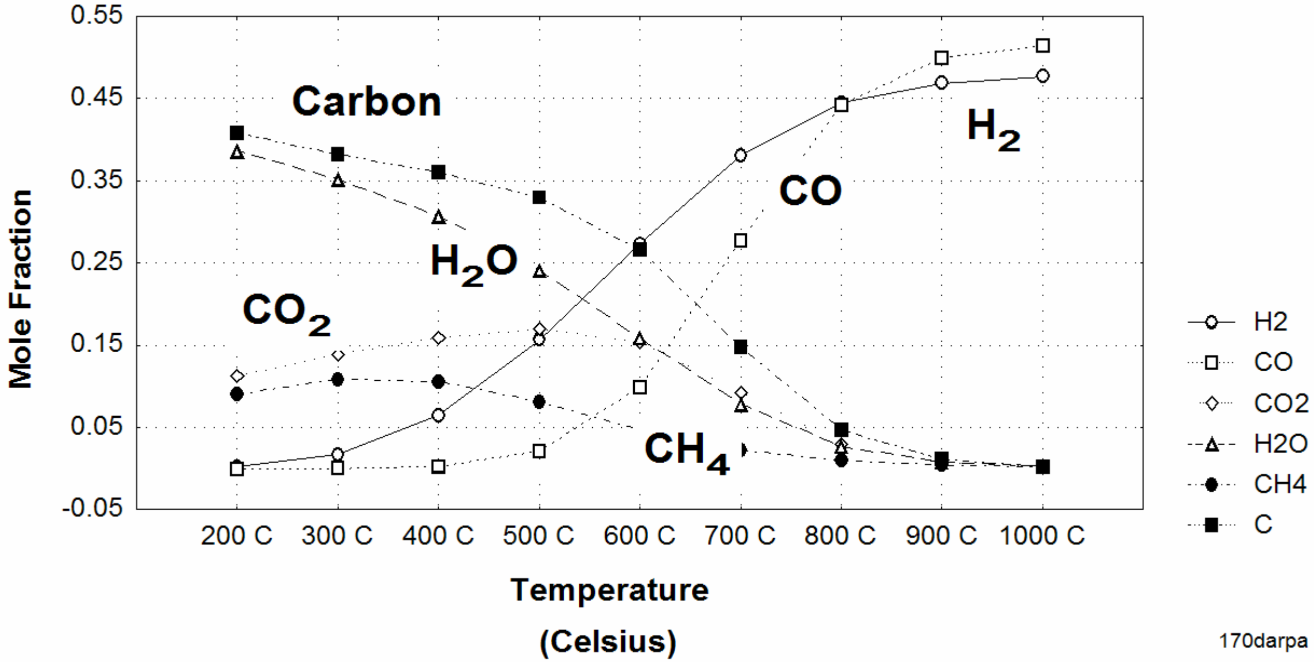
Direct Partial Oxidation of Methane Through a Steam Reforming Step

Steam Reforming	$CH_4 + H_2O\ (g) \rightarrow CO + 3H_2$	$\Delta H = +206.1\ kJ\ mol^{-1}$
Hydrogen Oxidation	$H_2 + O\ (ad) \rightarrow H_2O\ (g)$	$\Delta H = -241.8\ kJ\ mol^{-1}$
Oxygen Dissociation	$\frac{1}{2}\ O_2 \rightarrow O\ (ad)$	
Net Partial Oxidation	$CH_4 + \frac{1}{2}\ O_2 \rightarrow CO + 2H_2$	$\Delta H = -35.7\ kJ\ mol^{-1}$

- **Note: No net steam consumed.**

Thermodynamic Equilibrium Calculations for Reforming Diesel Fuel into CO + H_2 by Partial Oxidation

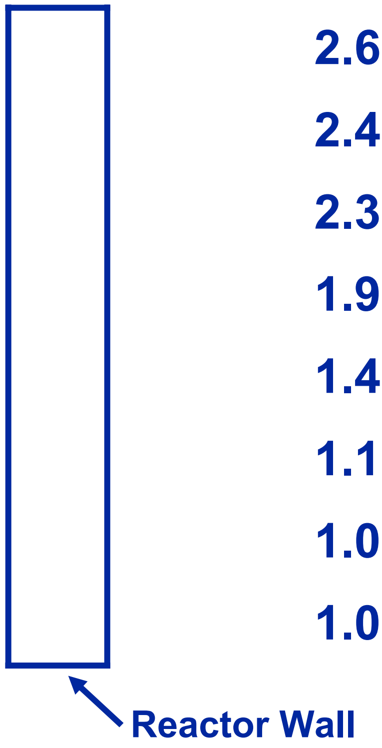
H : C : O Ratios Adjusted to 1.86 : 1 : 1.02



Results of thermodynamic equilibrium calculations predicting that H_2 and CO will be overwhelmingly favored above about 950°C-1000°C if one atom of oxygen is transported into the reactor for each atom of carbon in the diesel fuel. Calculations predict that at lower temperature deposition of carbon will be severe and that undesired deep oxidation products, CO_2 and H_2O, will form.

Local Atomic Ratio of Oxygen-to-Carbon Needed at Reactor Walls to Completely Suppress Formation of Carbon

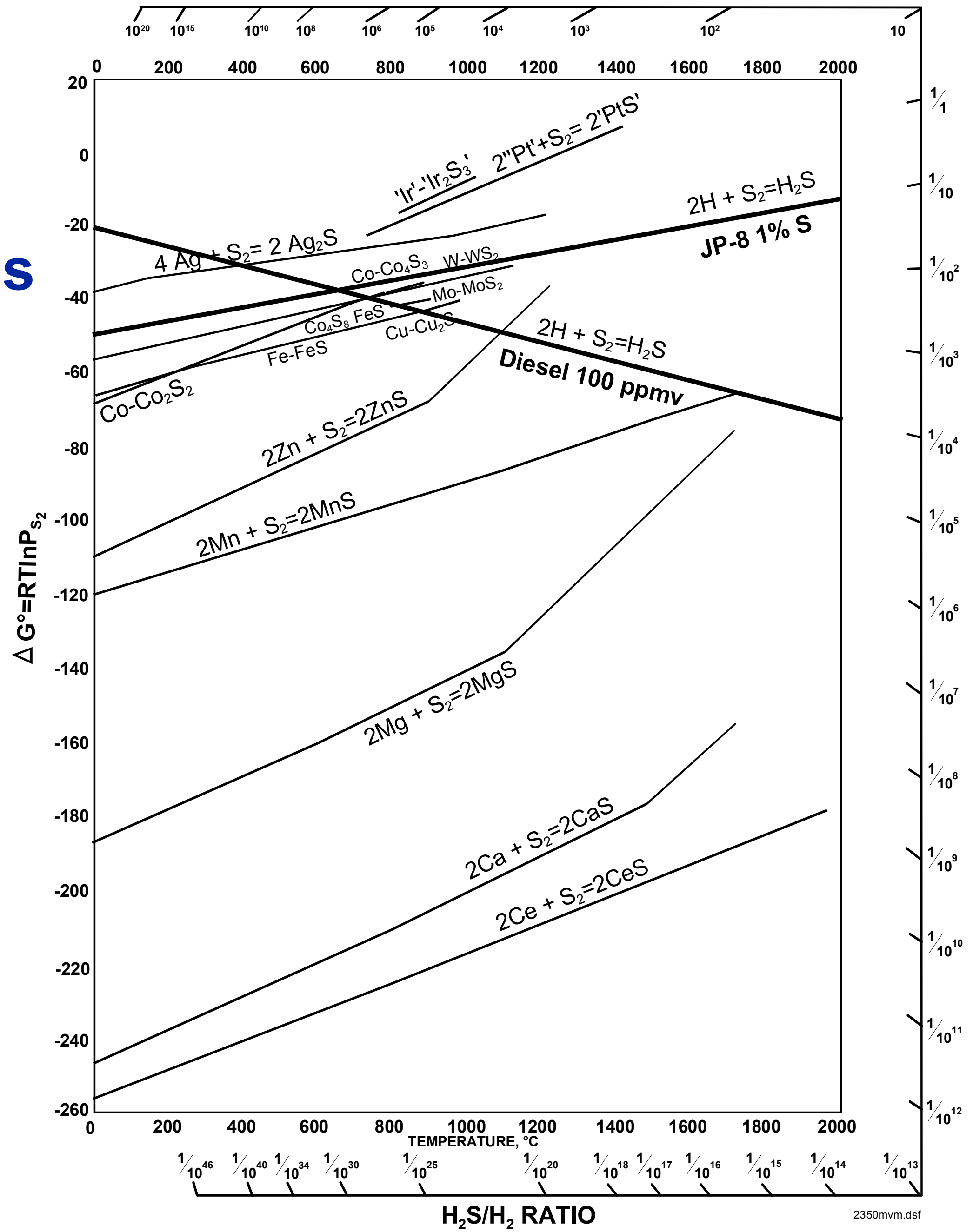
Temperature (°C)	Oxygen-to-Carbon Atomic Ratio
300	2.61
400	2.48
500	2.30
600	1.93
700	1.40
800	1.10
900	1.03
1000	1.02



- Assumes diesel fuel contains a hydrogen-to-carbon atomic ratio of 1.86-to-1.
- Assumes $1\text{x}10^{-45}$ moles carbon is negligible.

Ellingham Diagram Showing Relative Thermodynamic Stabilities of Metal Sulfides

- Most metals will form stable sulfides when exposed to >100 ppmv H_2S.
- Pt, Rh, Ir and Ag will remain metallic even with JP-8.
- Co, Cu and Fe will remain metallic if H_2 : H_2S ratio kept >10000 : 1.

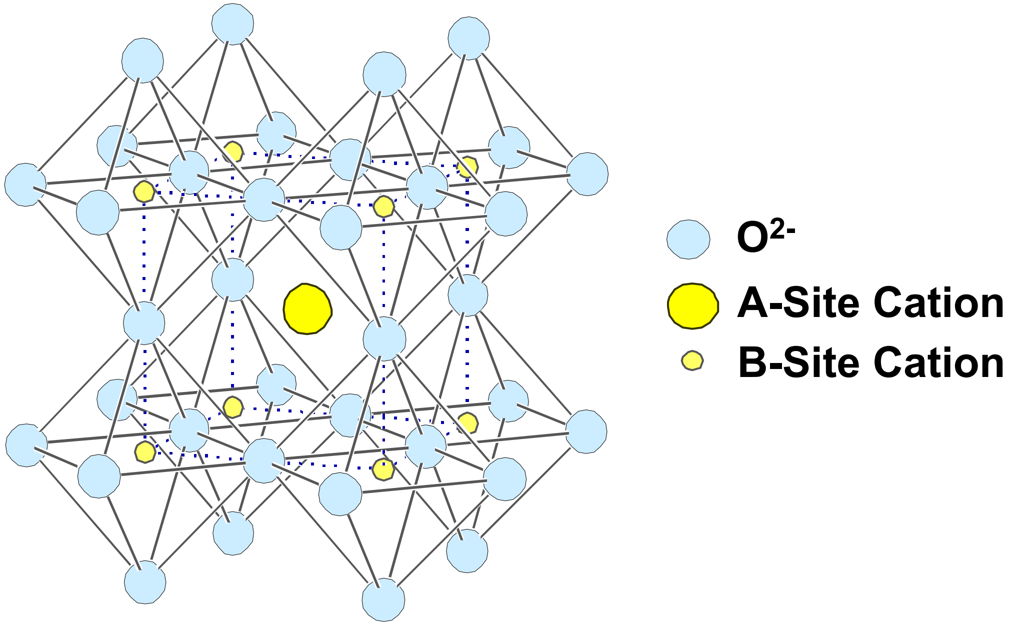


Some Options for Diesel Fuel Reforming Catalysts

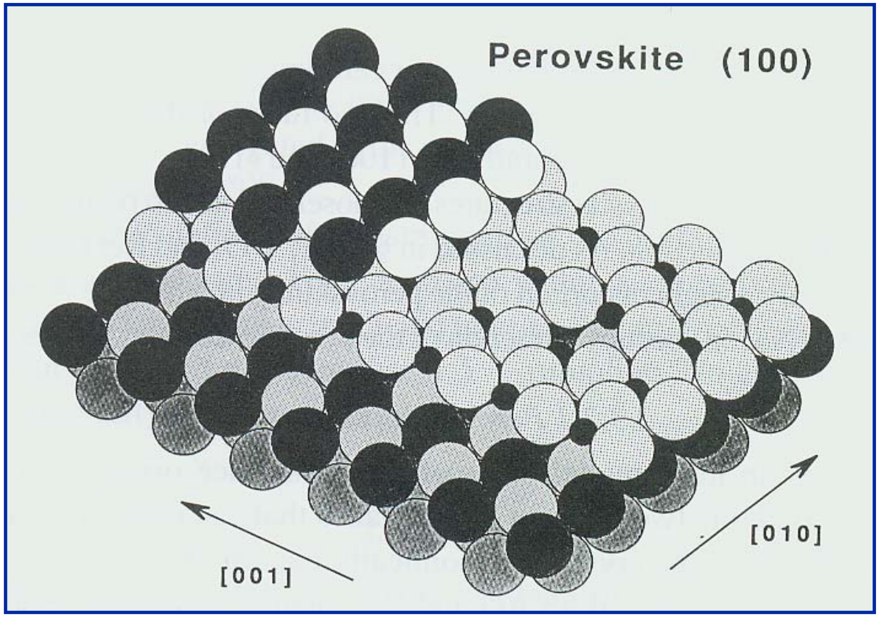
- Pt-Rh metal wire gauze
- Pt-Rh supported on yttria stabilized zirconia
- Pt-Rh supported on oxygen conducting perovskites
- Fe, Co (Ag, Cu)
- Oxygen conducting perovskites with Fe, Co, etc.

Note: Compounds of Ce, Ca, Mg possible adsorbents for removal of sulfur.

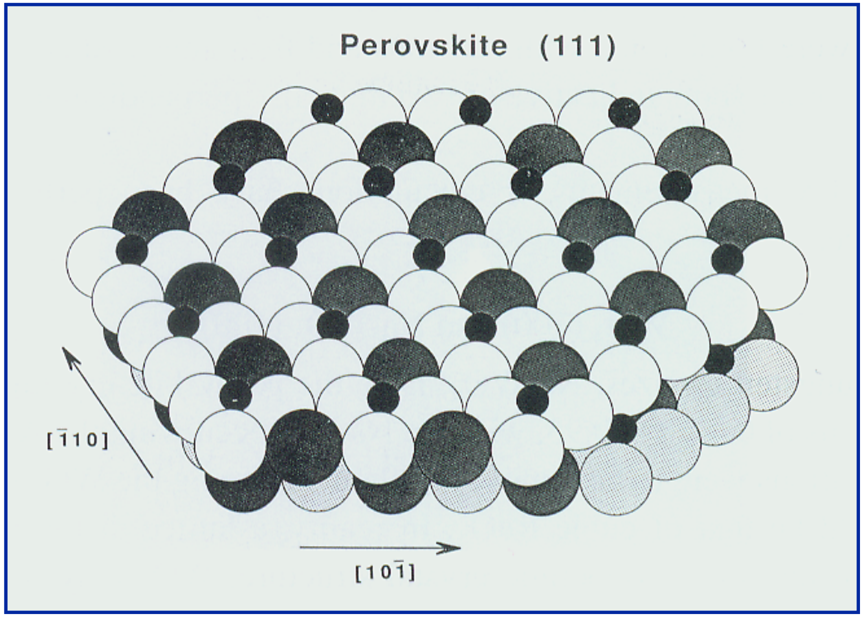
Crystal Structure of Eltron Patented Membrane of General Composition: $A_{1-x} A_x'B_{1-y}B_y'O_{3-\delta}$



Crystal structure of perovskite showing A- and B-site cations. Substances with this crystal structure are used in many oxidation catalysts. The ability of these materials to allow diffusion of oxygen through the crystal lattice by a vacancy hopping mechanism, provides a source of dissociated oxygen for oxidation reactions.



An ideal (100) surface of a perovskite catalyst crystallite. Note oxygen vacancy.



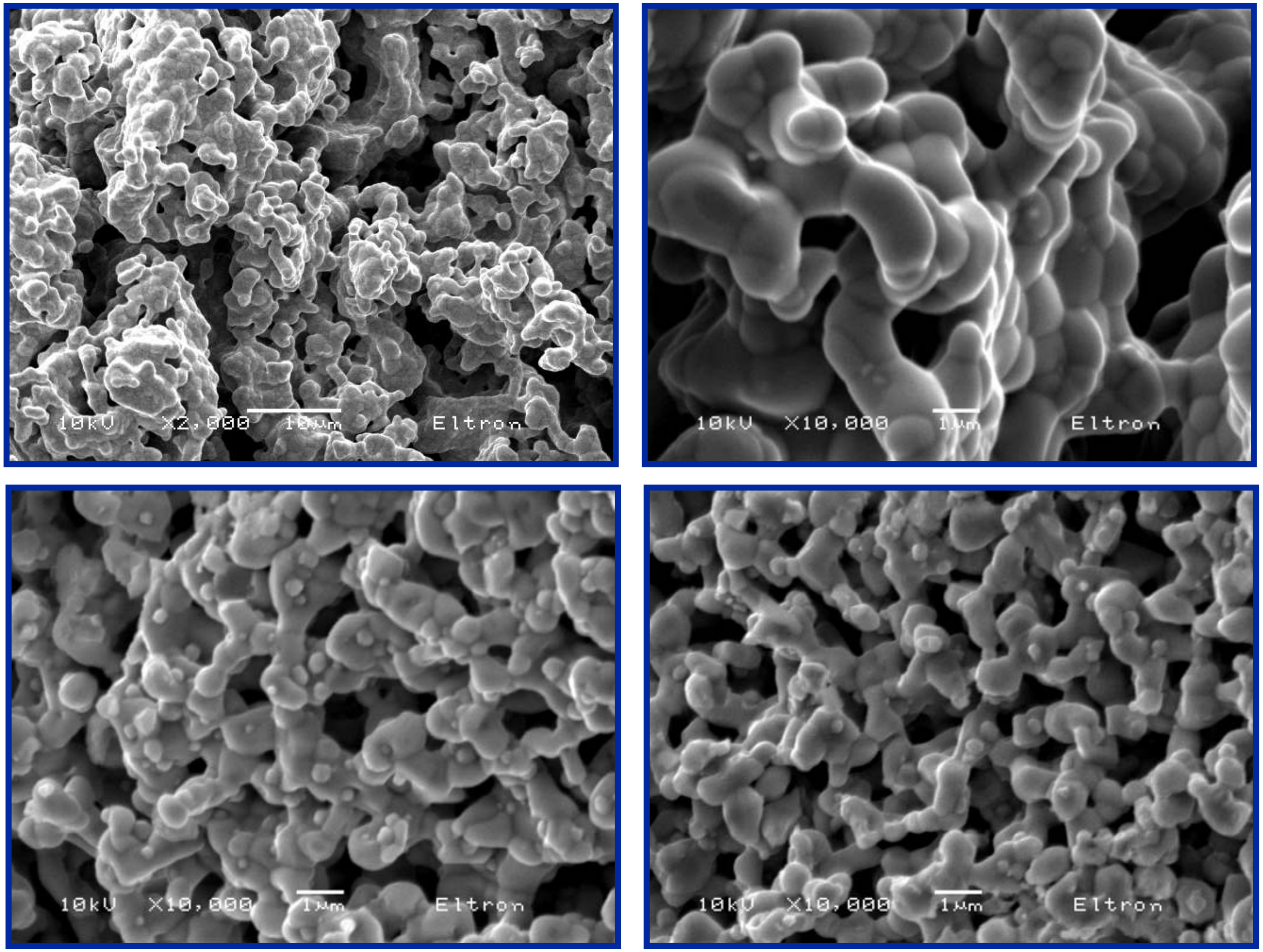
An ideal (111) surface of a perovskite catalyst crystallite.

Adapted from V. E. Henrich and P. A. Cox, “The Surface Science of Metal Oxides.”

Partial List of Catalysts Formulated and Tested during Phase I

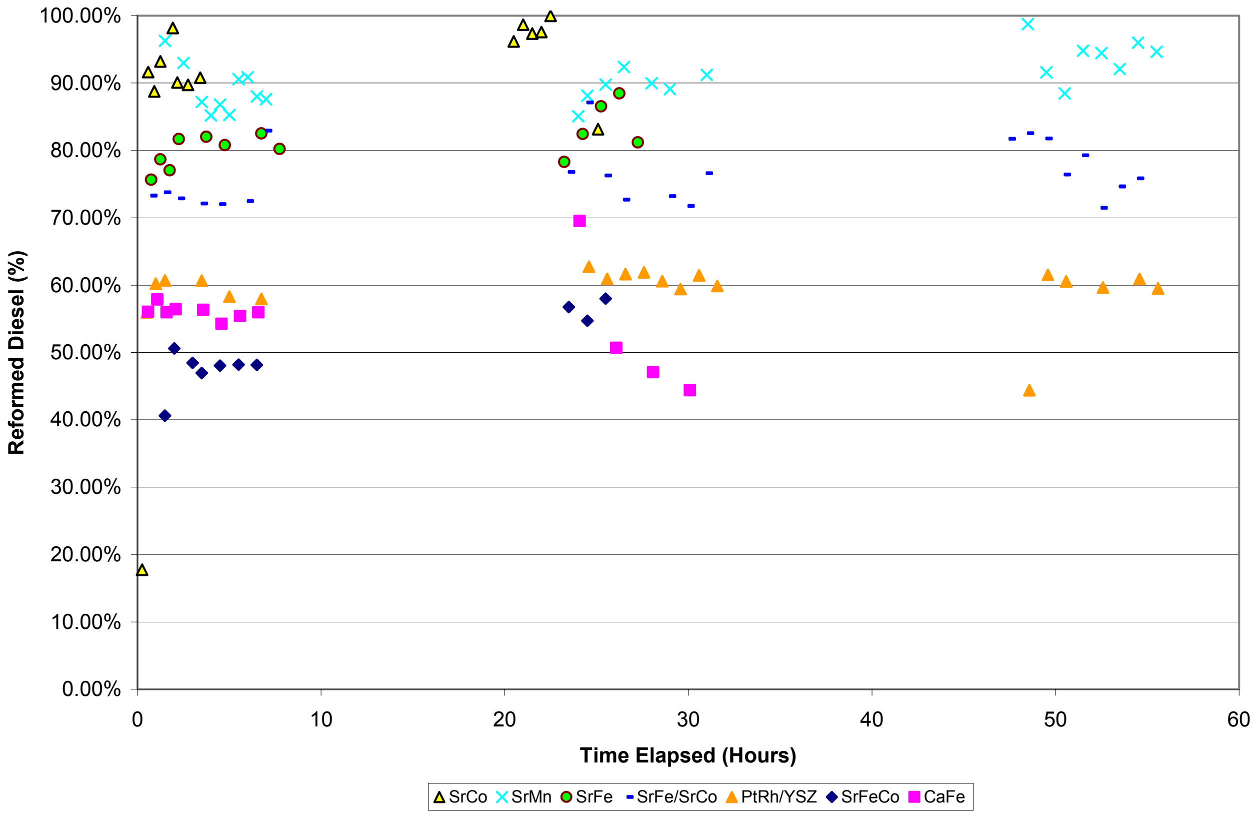
Composition
$La_{1-x}Sr_xFeO_{3-\delta}$
$La_{1-x}Sr_xCo_{1-y}Mn_yO_{3-\delta}$
$La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$
$La_{1-x}Ca_xFeO_{3-\delta}$
$La_{1-x}Sr_xFe_{1-y}Ru_yO_{3-\delta}$
$BaCe_{1-y}Y_yO_{3-\delta}$
$BaCe_{1-y}Co_yO_{3-\delta}$
$BaCe_{1-y}Fe_yO_{3-\delta}$
$La_{1-x}Sr_xCoO_{3-\delta}$
$La_{1-x}Sr_xMnO_{3-\delta}$
$La_{1-x}Ca_xCoO_{3-\delta}$

Perovskite Catalysts

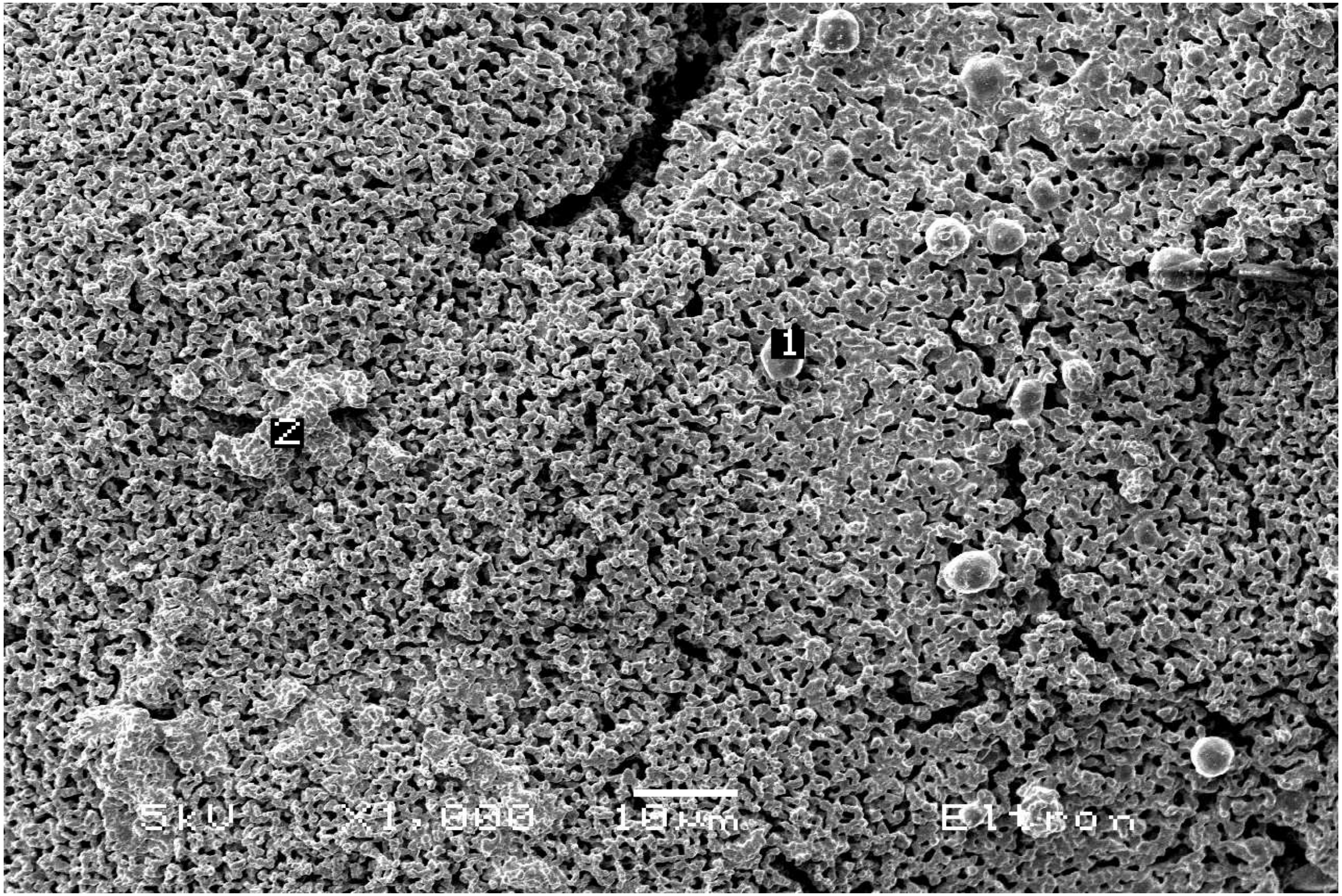


Upper: Single phase perovskite; Lower: Two phase perovskite

Percent Diesel Fuel Reformed as a Function of Time; 1273K; Unsupported Perovskite Catalyst Bed

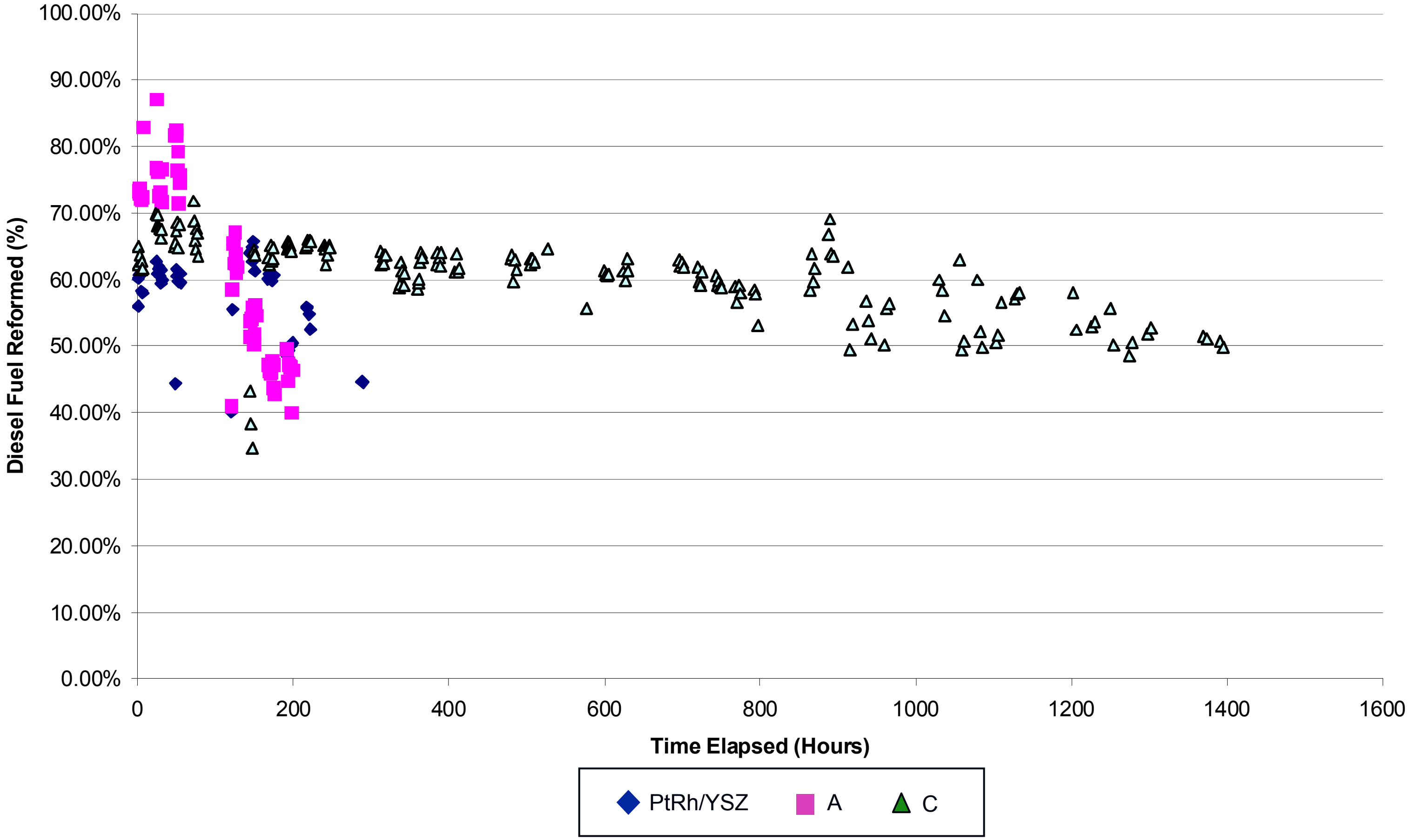


Summary of relative catalyst activity for diesel fuel reforming of unsupported perovskite catalyst beds and supported Pt-Rh/YSZ tested at 1000°C. Percent diesel fuel reformed is based upon known moles of C entering the reactor and the CO, CH_4 and CO_2 detected exiting the reactor. Selectivity: A - CO 84.6%, CO_2 2.8%, CH_4 12.6%, C - CO 73.8%, CO_2 14.7%, CH_4 11.5%.



SEM image of metal catalyst spheres (indicated by #1) leading to loss of metal catalyst surface area after 120 hours at 1000^{o}C.

Two Month Test: Percent Diesel Reformed as a Function of Time; 1273K



Result of a long-term test at 1000°C under commercial diesel fuel reforming conditions. Comparison of Pt-Rh/YSZ to perovskite based catalysts.

Phase II Plans

- Level of effort $750,000; two years
- Minimize use of noble metals in diesel reforming catalysts
- Fabricate prototype of catalytic membrane reactor with self-cleaning reactor walls
- Minimize nitrogen in reactor with oxygen transport membranes