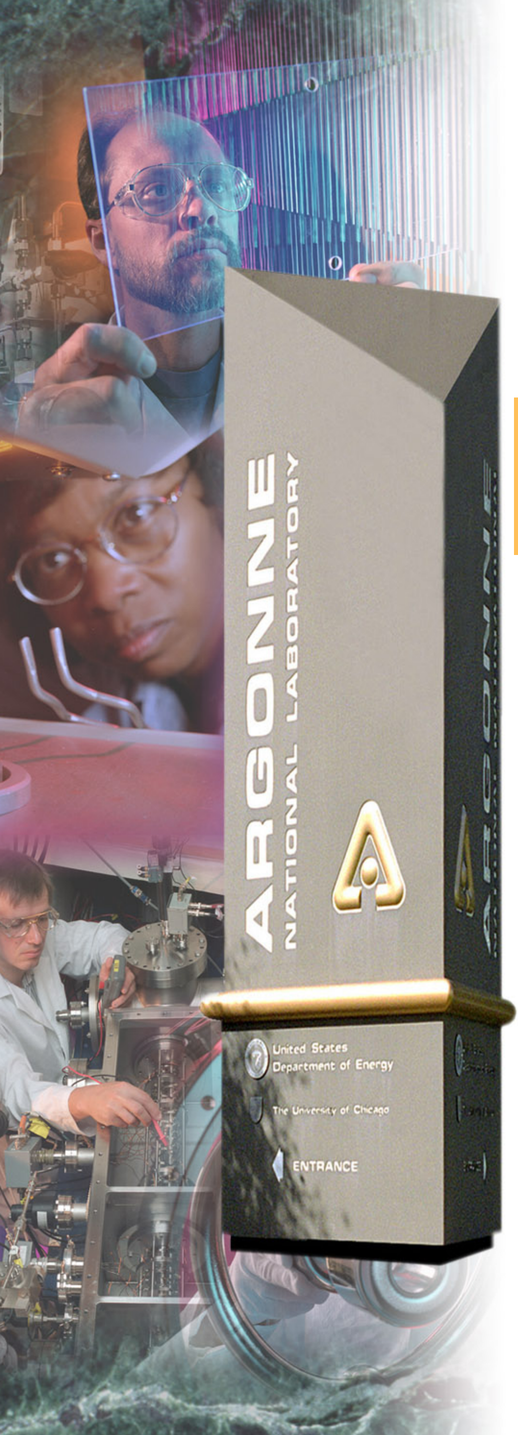

CORE Technology Developments at Argonne

By
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6th SECA Annual Workshop
April, 2005

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

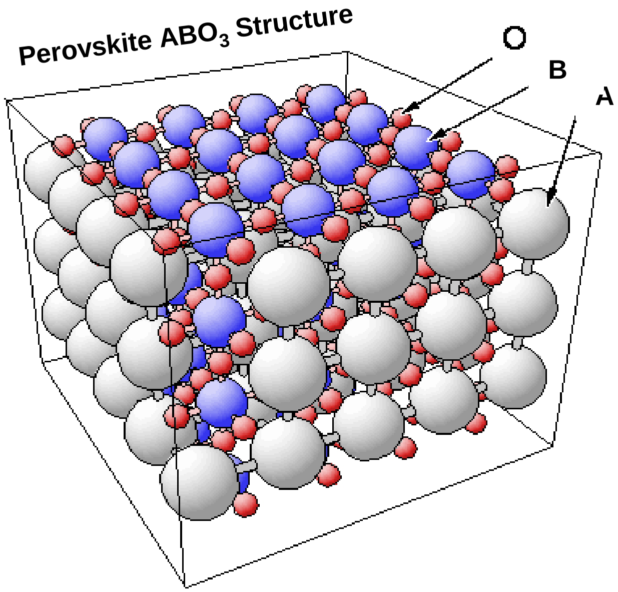
Scope

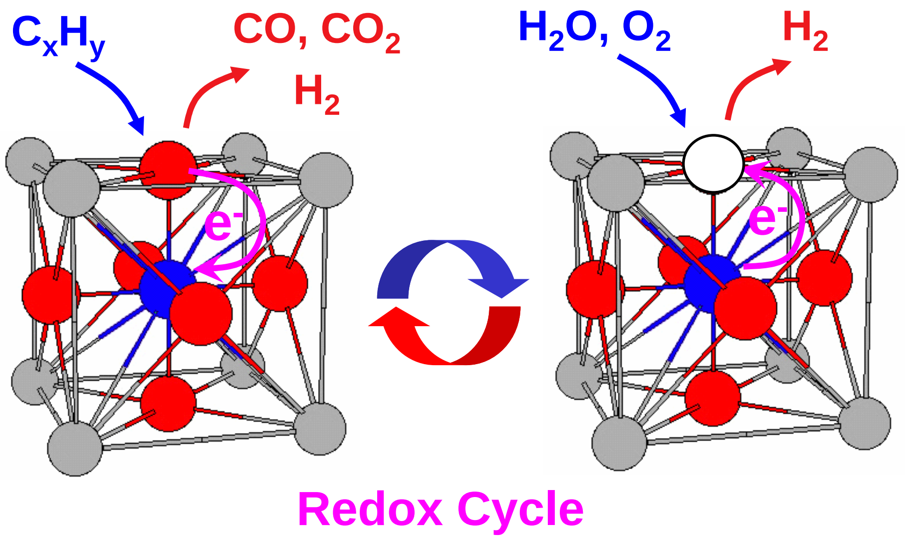
- **Investigate Bipolar Plate Interactions with Cathode Materials**
- **Develop new Diesel Reforming Catalysts**

Why do we need new Diesel reforming catalysts?

- **Nickel on alumina and Rhodium on oxide support evaporate and consolidate**
- **Nickel, and to a lesser extend, Rhodium adsorb sulfur compounds and deactivate**
- **Poly-aromatic compounds in Diesel react more slowly and block the catalytic sites**

- **The Perovskite Matrix…**
  - Does not adsorb sulfur compounds.
  - Is stable under high temperature & redox environment.
  - Can exchangeable *A & B* site elements



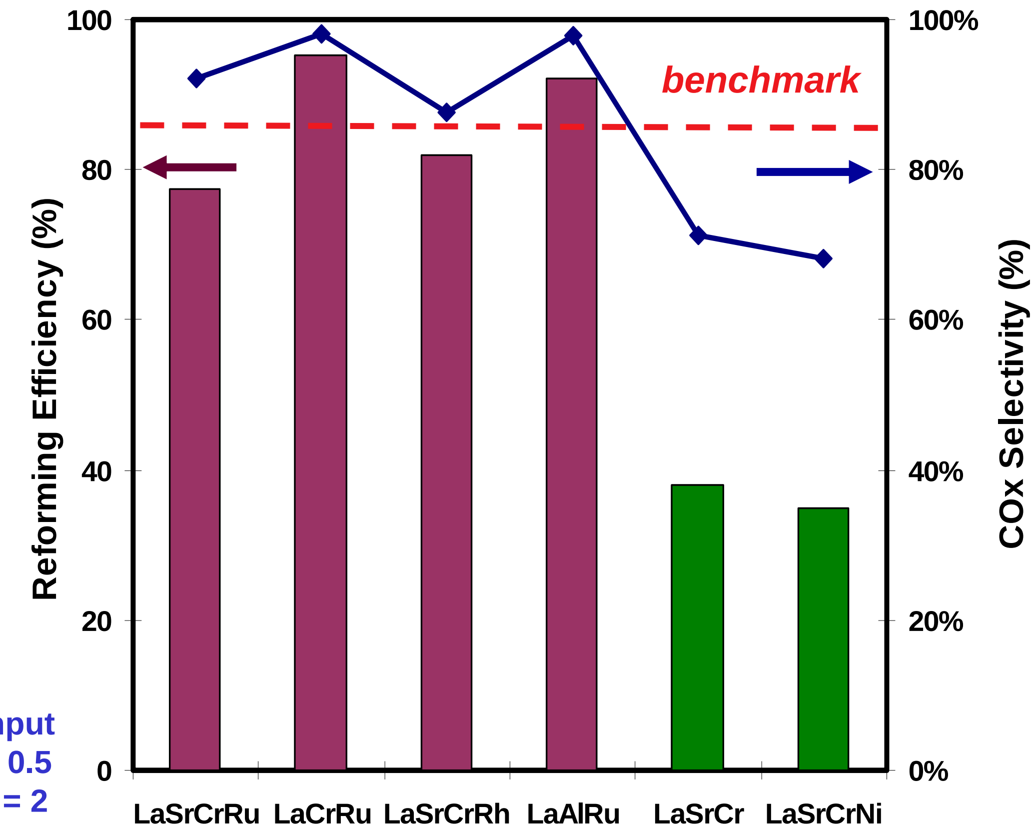


Conductivities of both e^- and $V_O^{\cdot\cdot}$ of perovskite expand the catalytic active site through electron and oxygen vacancy transfers in a redox process.

B-site doping of LaCrO3 creates effective catalysts

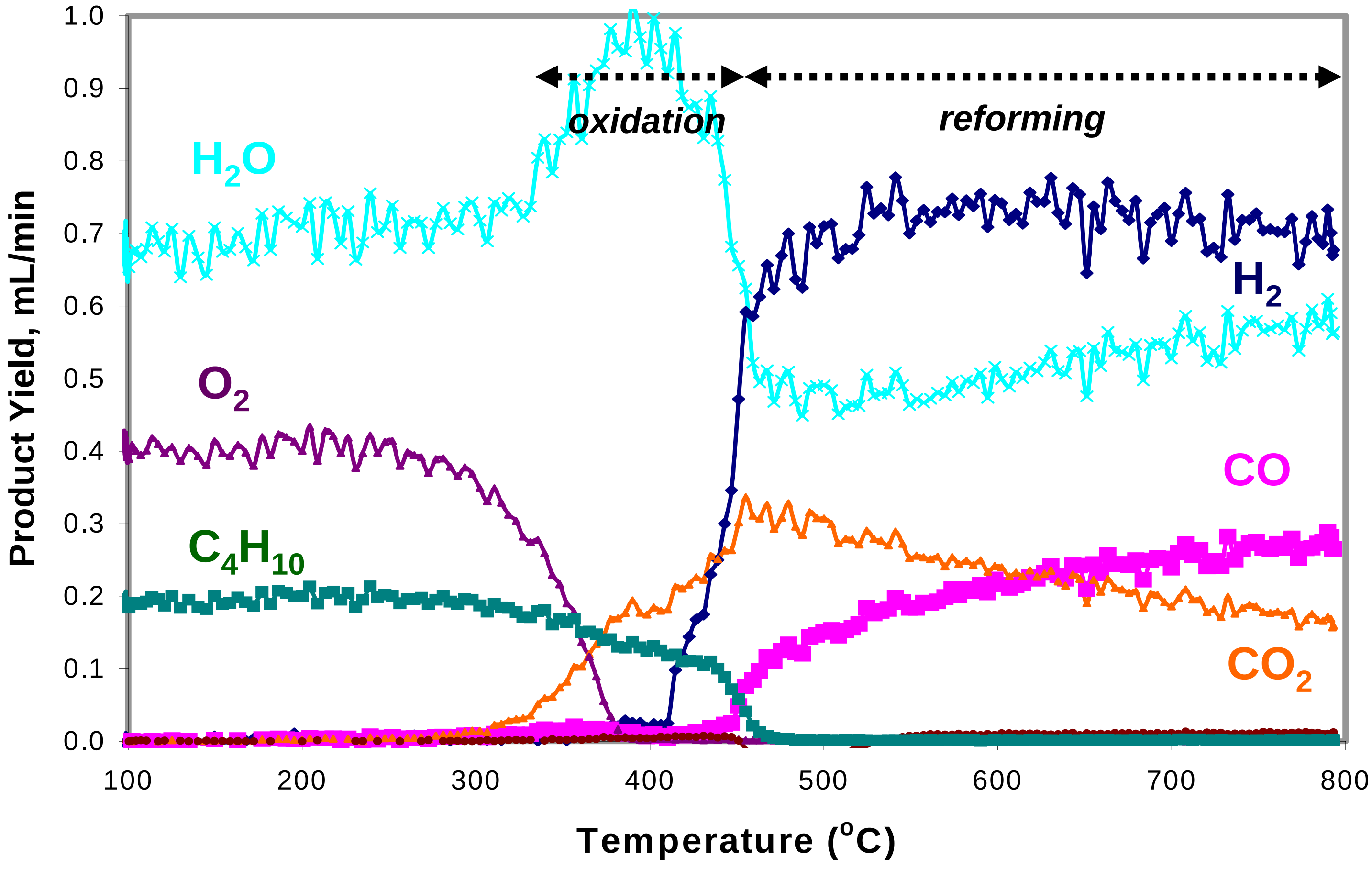
- **Exchanging B site with 5% Ru or Rh significantly improves reforming efficiency and COx selectivity.**
- **New perovskites approach or exceed supported Rh in catalytic activity.**

Comparison of B-site dope vs. non-doped perovskites



ATR input
$O_2/C = 0.5$
$H_2O/C = 2$

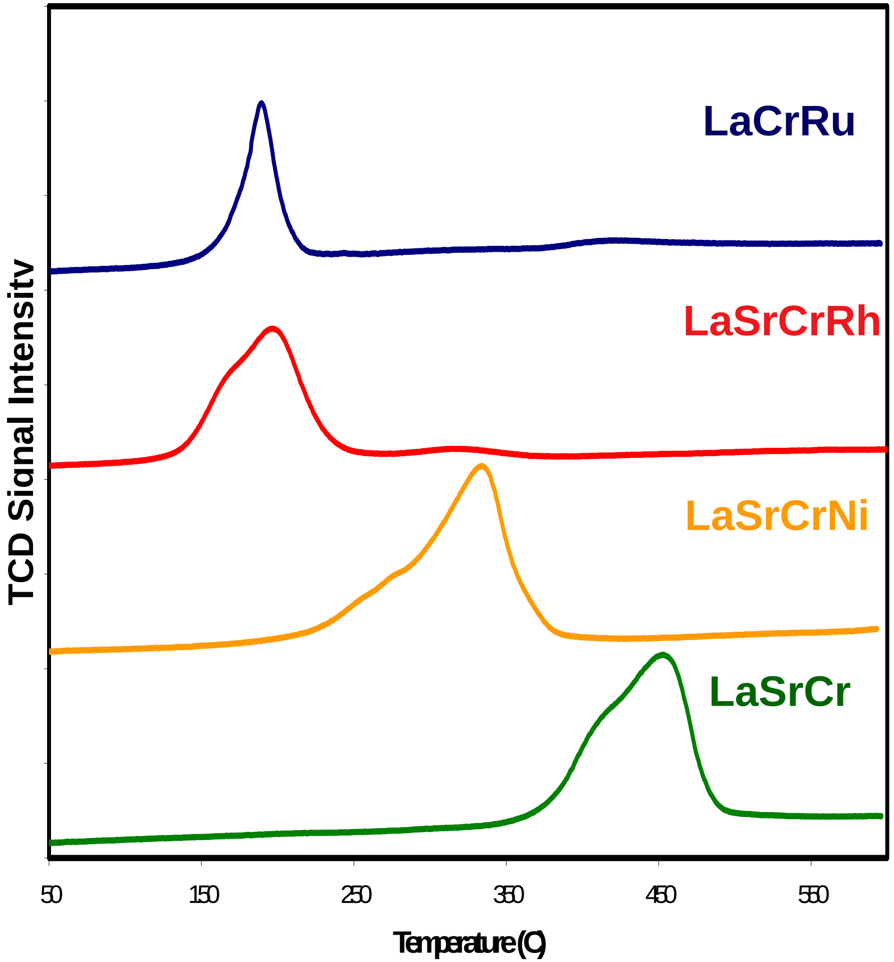
Temperature programmed reforming on a LaSrCrRu catalyst



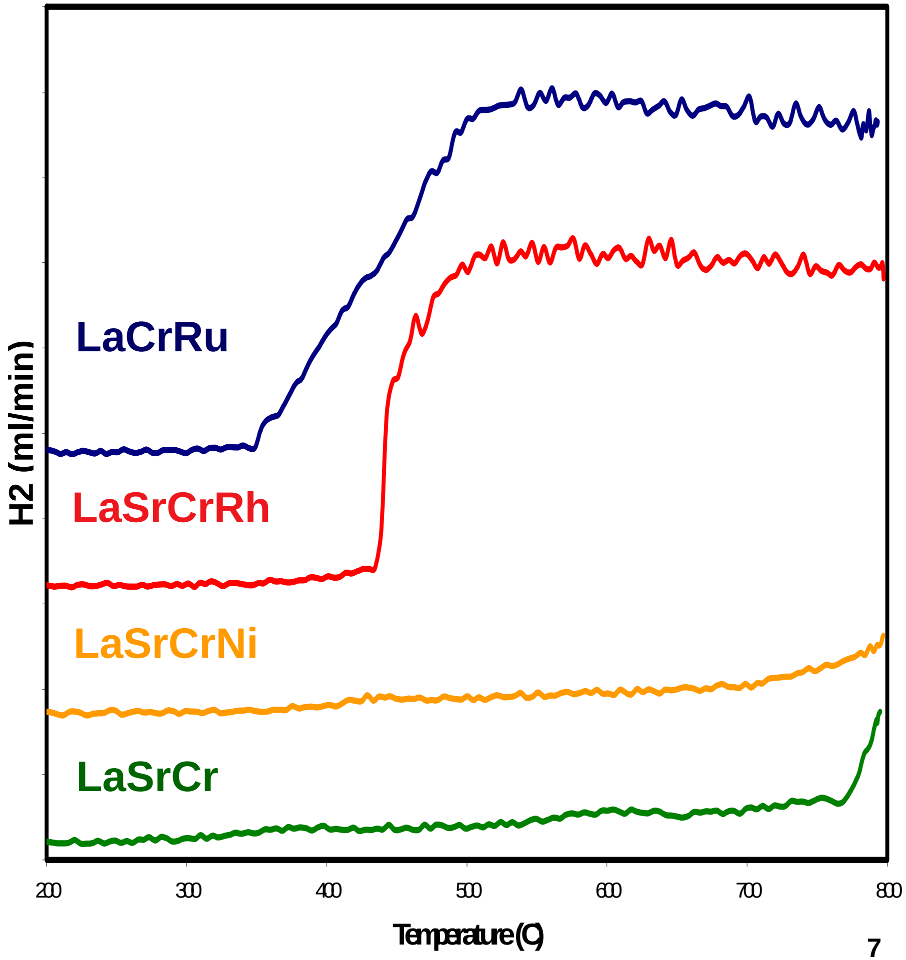
Ru doped perovskites demonstrate low light-off temperature for hydrogen production

TPR and light-off studies suggest dopant reduction as key step in redox process

H_2-TPR study revealed lower reduction temperature for PM doped perovskites….

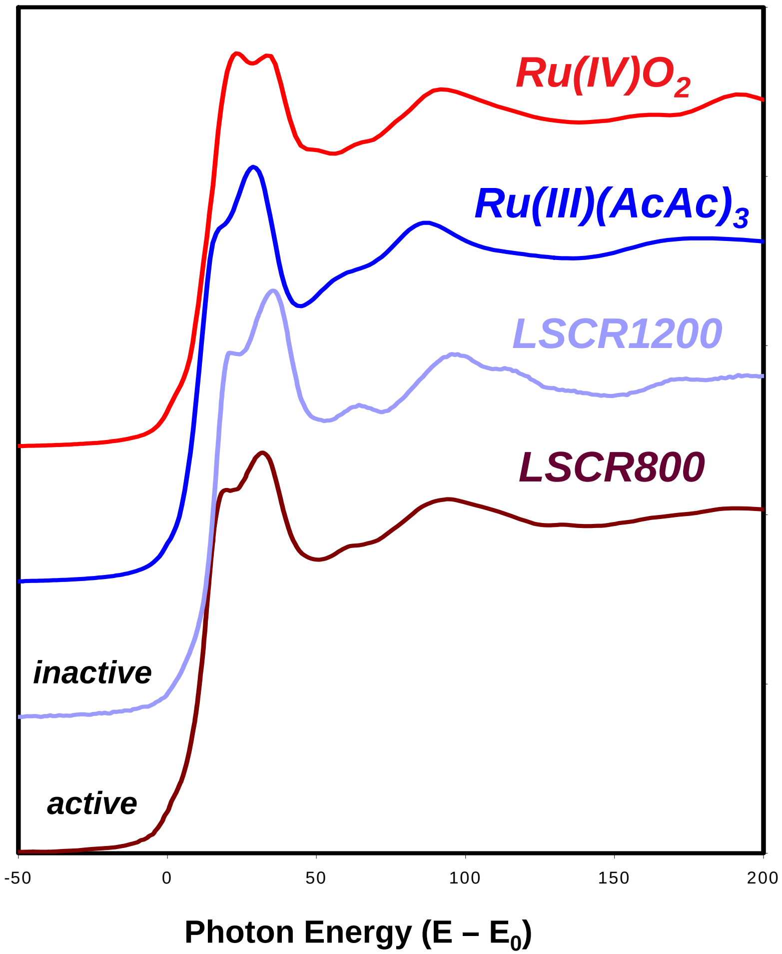


Same catalysts showed lower T-lightoff & broader operating window in C_4H_{10} ATR study.

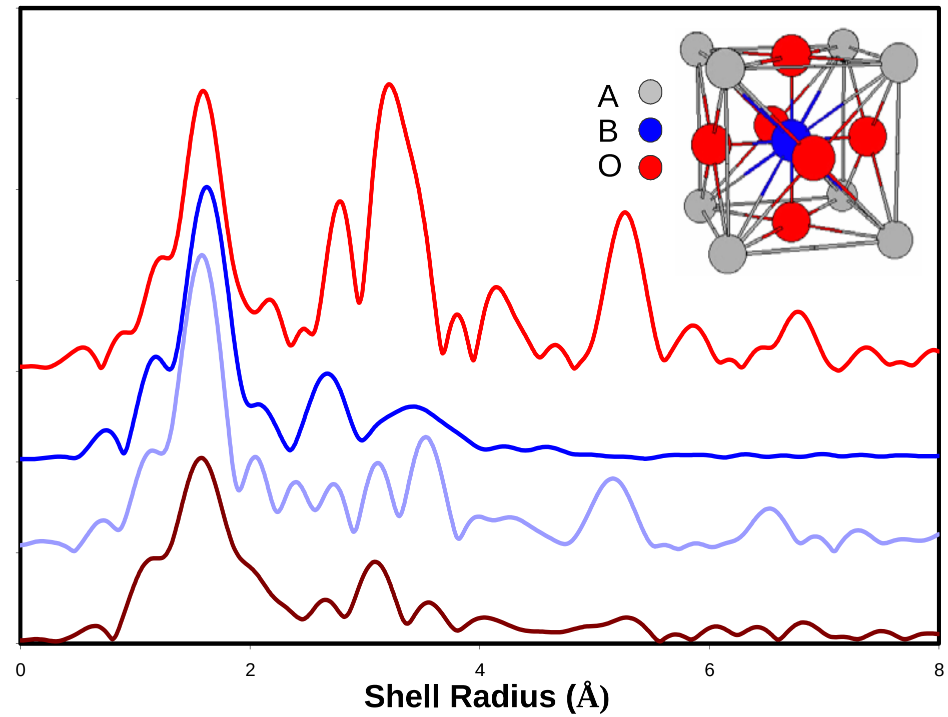


XANES & EXAFS identify local structure & valance of exchanged B-site dopant in perovskites

XANES identified Ru in chromite is in +3 valance state….



EXAFS found Ru atomically dispersed with increased CN at higher calcination temperature.

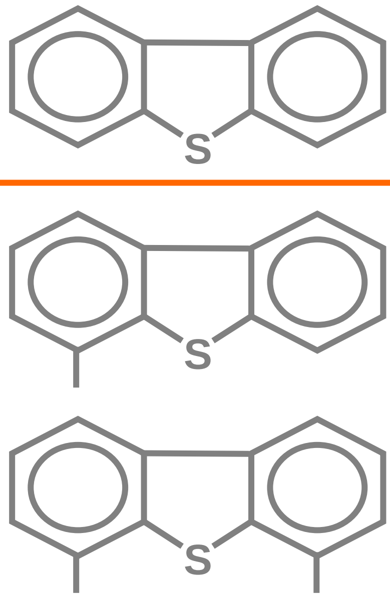


	N	*R (Å)*	σ^2
LSCR1200	6.0	1.943	$2.5x10^{-5}$
LSCR800	4.7	1.953	$2.5x10^{-5}$

Sulfur has a tolerable effect on the catalytic activity

Dibenzothiophene (DBT) and its derivatives are difficult to be removed from diesel through HDS process …

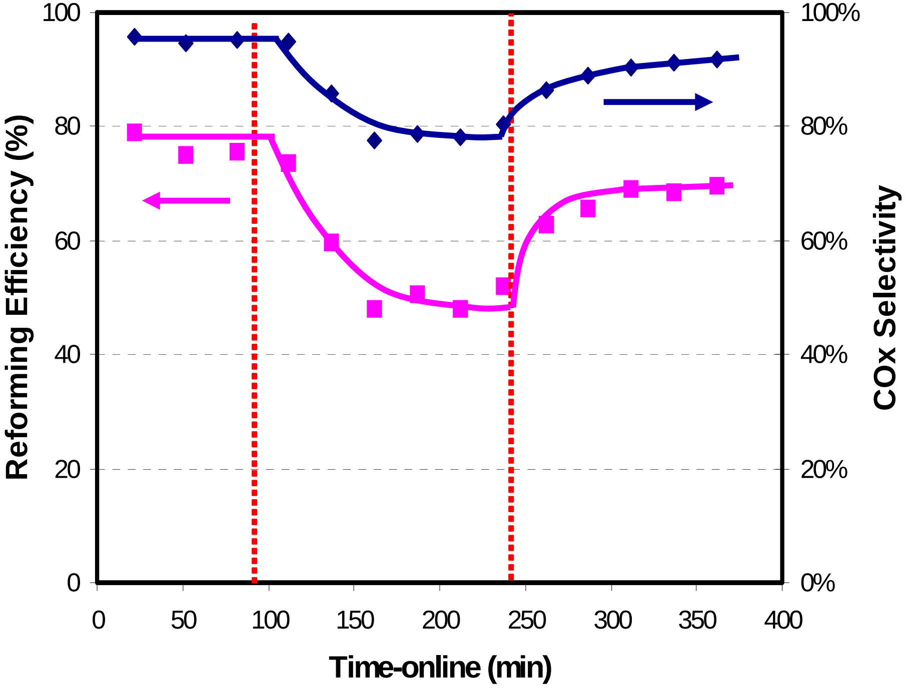
Introducing 50 ppm sulfur in the form of DBT temporarily suppress reforming efficiency and COx selectivity.



DBT

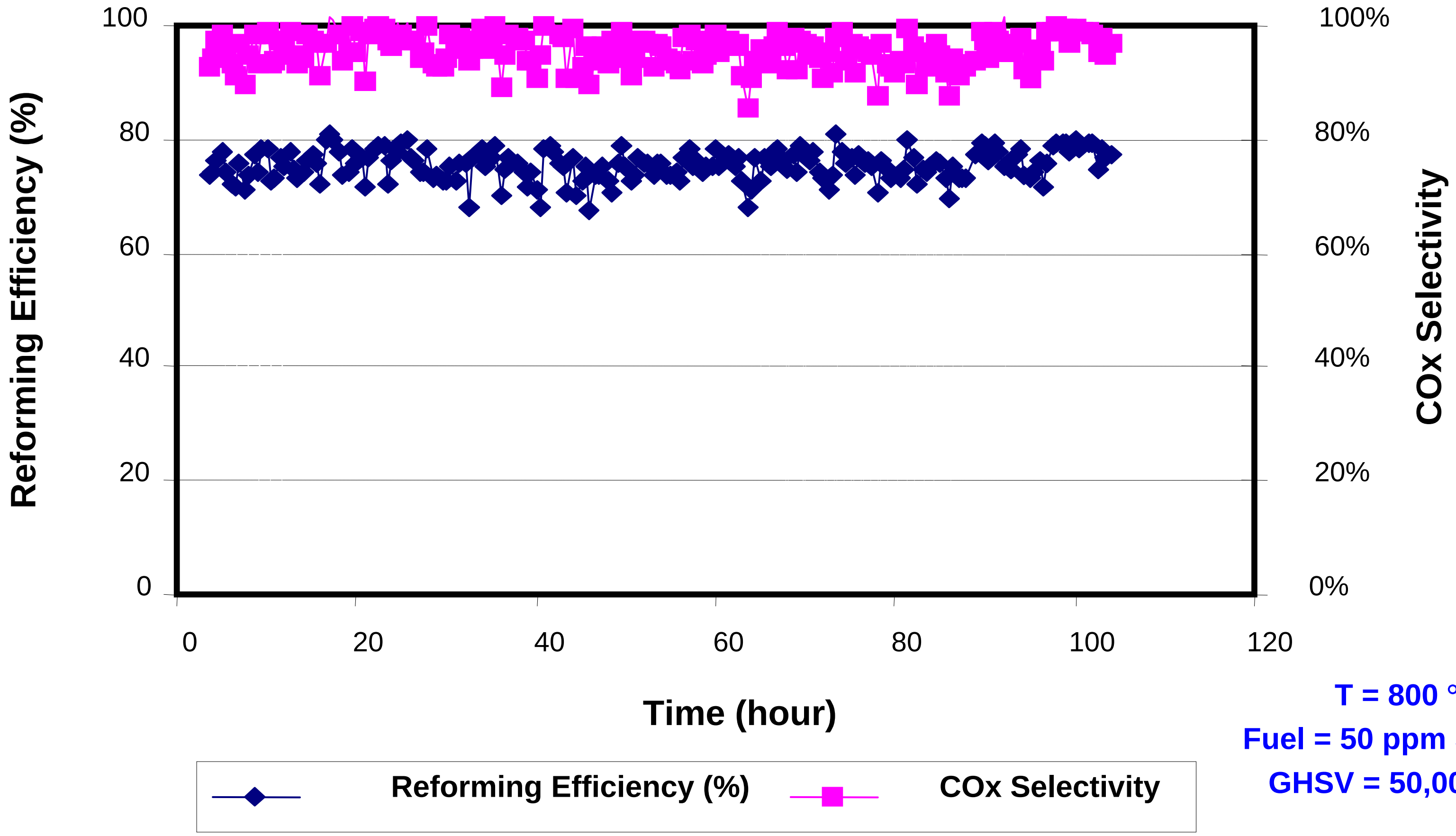
4-MDBT

4,6-DMDBT



Catalyst re-activates after S is removed from fuel.

Stable reforming observed during 100-Hr aging test with 50 ppm S in DBT



T = 800 °C
Fuel = 50 ppm $S/C_{12}H_{26}$
GHSV = 50,000 hr-1

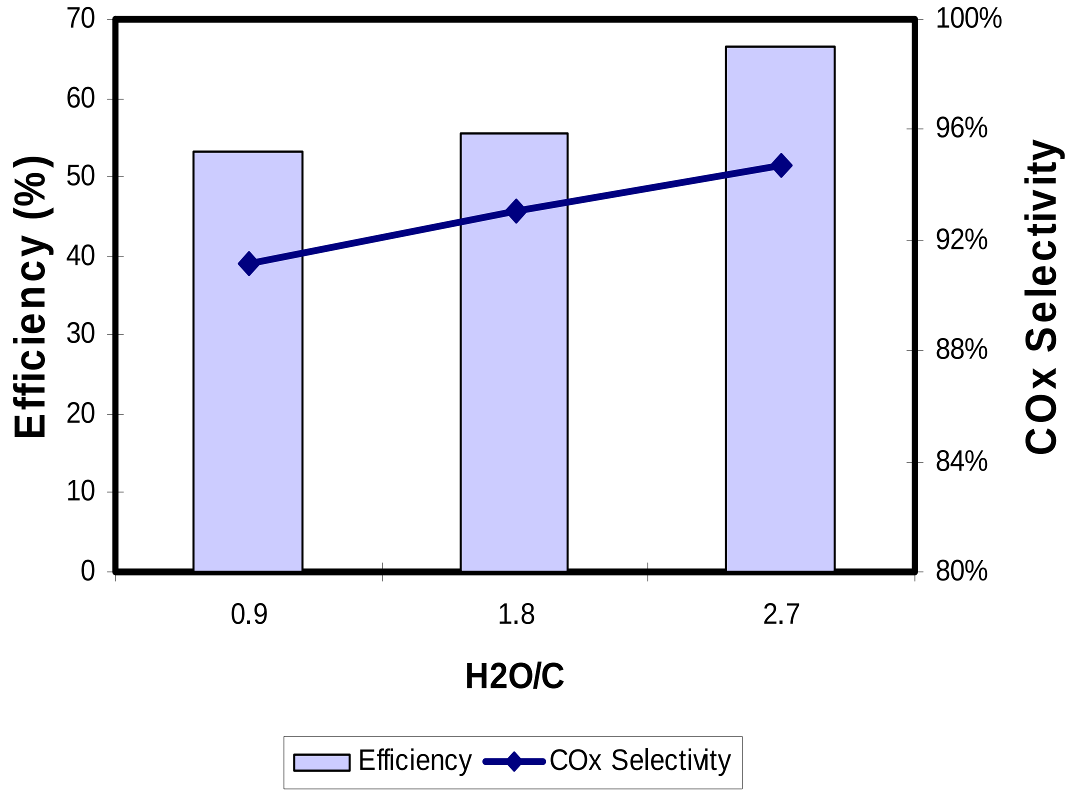
Excellent catalytic stability was observed during 100 hour aging test with S contaminated fuel

Reforming of a Surrogate Diesel Fuel

Space velocity: 86000 hr^{-1}

Temperature 800°C

40%	**Dodecane**
25%	**Butylcyclohexane**
20%	**Decalin**
7%	**Butylbenzene**
5%	**Tetraline**
3%	**1-Methylnaphtalene**
0.29%	**Dibenzothiophene**



Future plans for catalyst development

- Conduct 1000 hour life test
- Test catalyst on actual Diesel fuel
- Explore sequential recycling of vent gas
- Extend single site catalysis concept to other compounds
- Transfer technology to vertical teams

Chromium Oxyhydroxide Formation

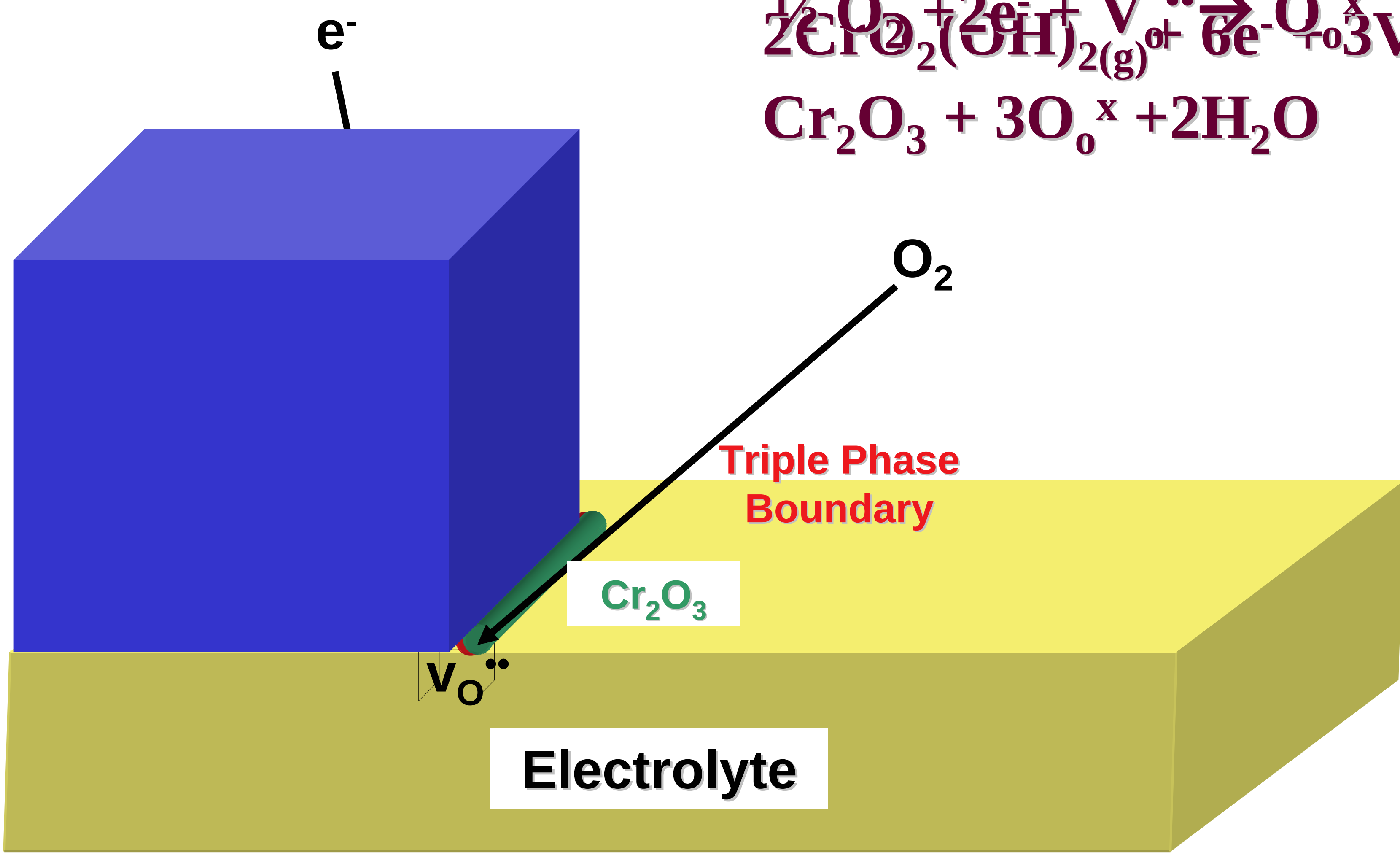
$$2Cr + 1.5O_2 \rightarrow Cr_2O_3$$

$$Cr_2O_3 + O_{2(g)} + H_2O_{(g)} \rightarrow 2CrO_2(OH)_{2(g)}$$

Electronically Conducting Cathodes

$$\tfrac{1}{2} O_2 + 2e^- + V_o^{\bullet\bullet} \rightarrow O_o^x$$

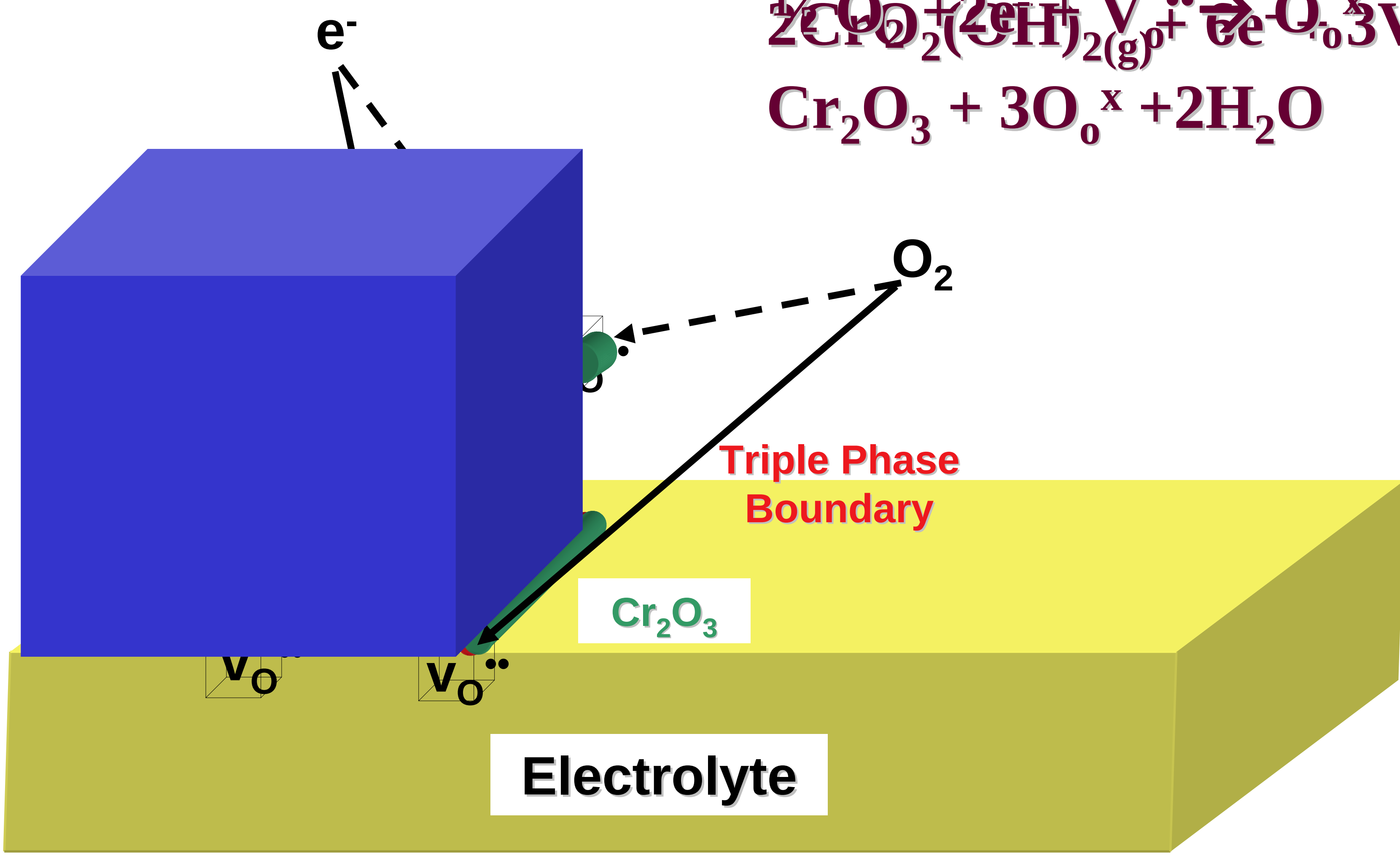
$$2CrO_2(OH)_{2(g)} + 6e^- + 3V_o^{\bullet\bullet} \rightarrow Cr_2O_3 + 3O_o^x + 2H_2O$$



Mixed Conducting Cathodes

$\frac{1}{2} O_2 + 2e^- + V_o^{\bullet\bullet} \rightarrow O_o^x$

$2CrO_2(OH)_{2(g)} + 6e^- + 3V_o^{\bullet\bullet} \rightarrow Cr_2O_3 + 3O_o^x + 2H_2O$

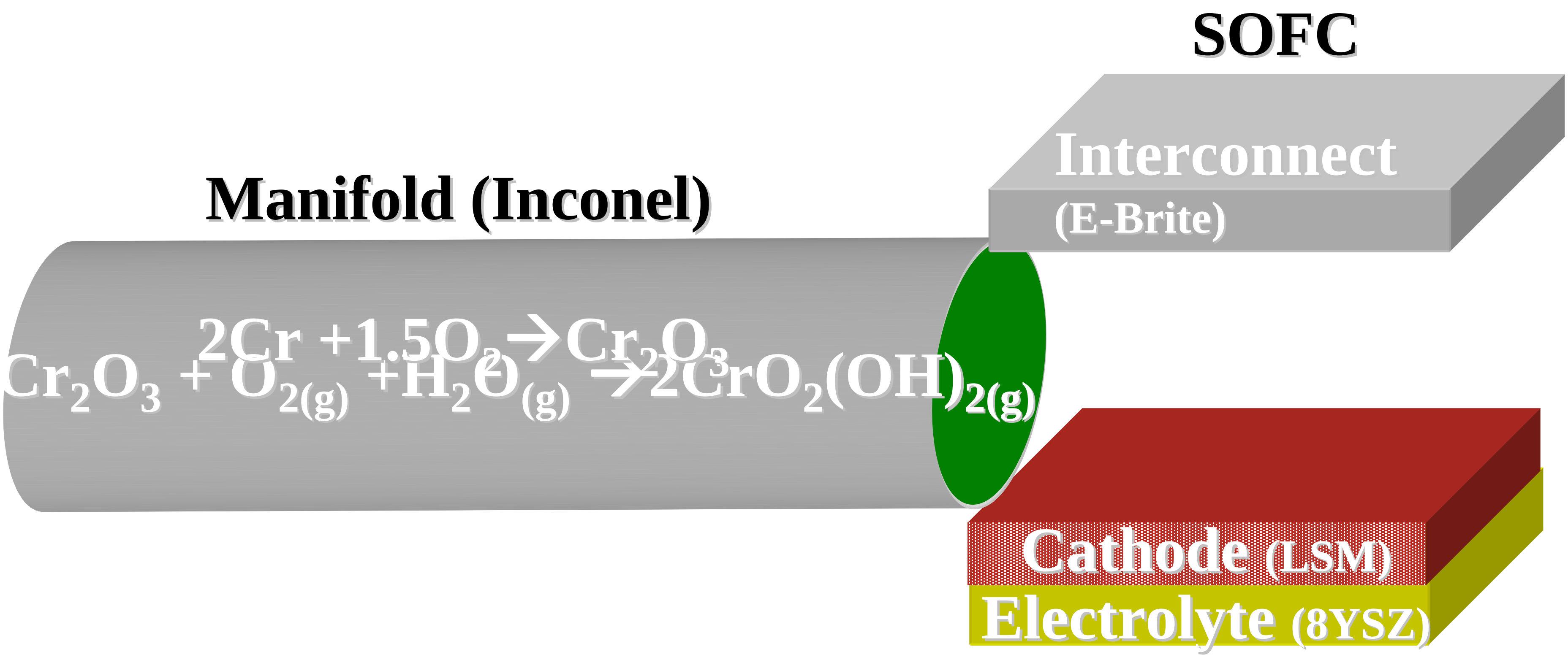


Summary of Cell Tests with Crofer

- **Cr content highest at cathode/electrolyte interface**
- **Cr throughout the LSF and LSF_{sub}**
- **Cr content correlates with oxygen ion vacancy concentration**
  - LSM < LSF < LSF_{sub}

$$2CrO_2(OH)_{2(g)} + 6e^- + 3V_o^{\bullet\bullet} \rightarrow Cr_2O_3 + 3O_o^x + 2H_2O$$

Where is the chromium coming from?



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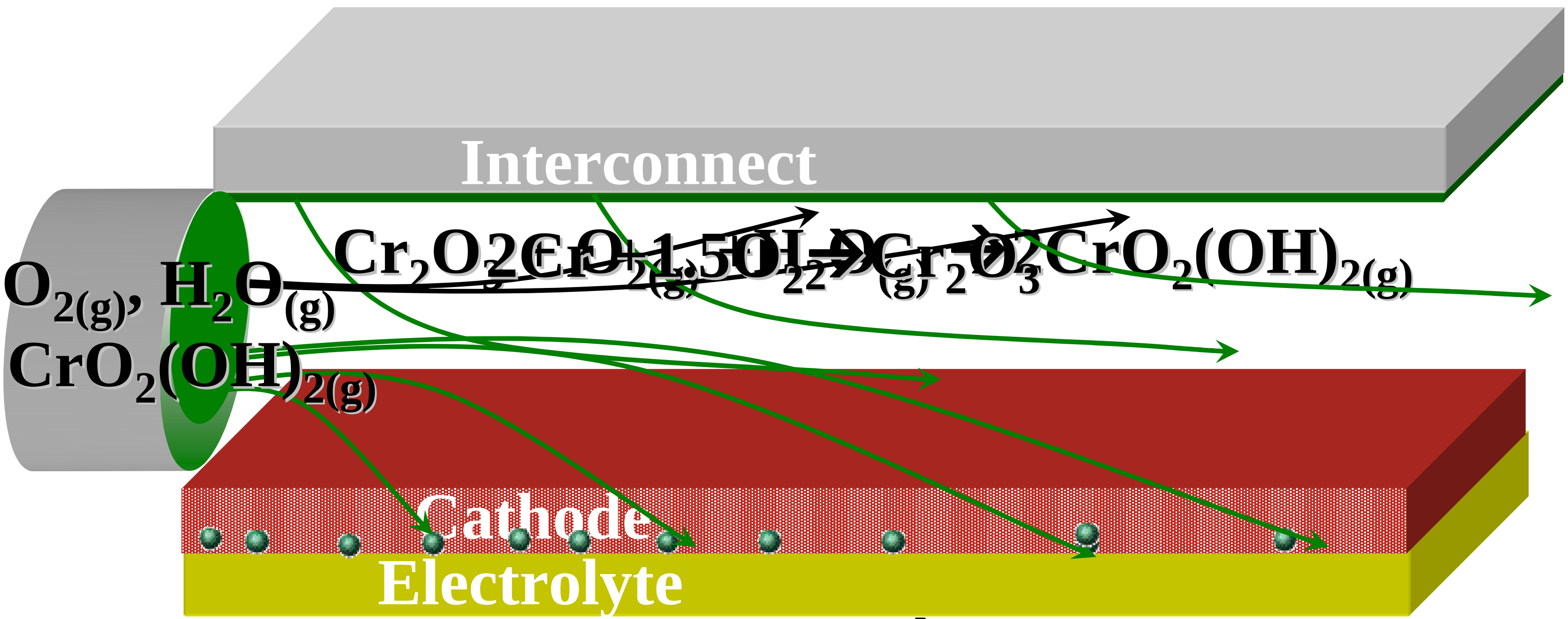
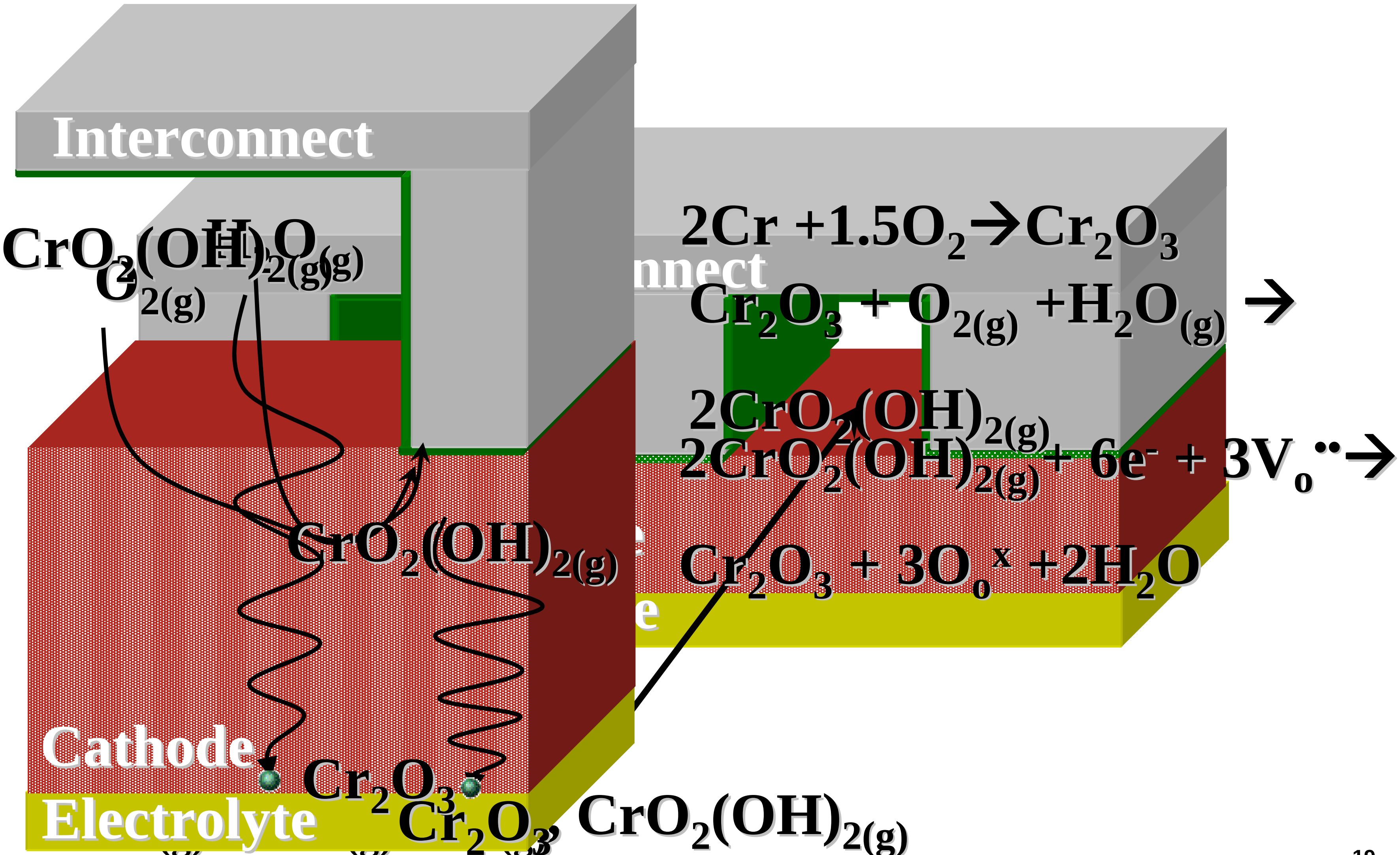


$$2CrO_2(OH)_{2(g)} + 6e^- + 3V_o^{\bullet\bullet} \rightarrow Cr_2O_3 + 3O_o^x + 2H_2O$$

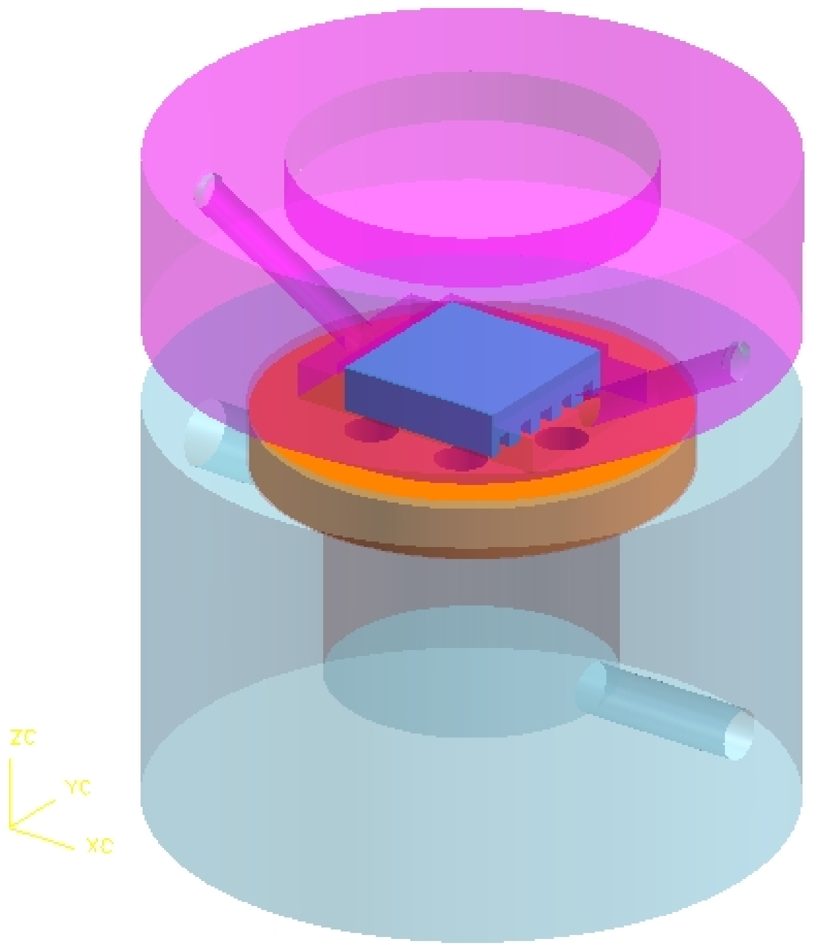
Conceivable Chromia Depositions



Future plans for chromium interactions

- **Operate lab scale cells with ribbed current collectors**
- **Look for chromia deposits in cathode along flow-channels and under ribs**
- **Co-operate with PNNL on defining sources of chromium**

Schematic of a Fixture with ribbed Flowfield



Acknowledgements

- **This work was supported by the U.S. Department of Energy, Office of Fossil Energy – Solid State Energy Conversion Alliance , Program Managers, Dr. Lane Wilson and Magda Rivera**