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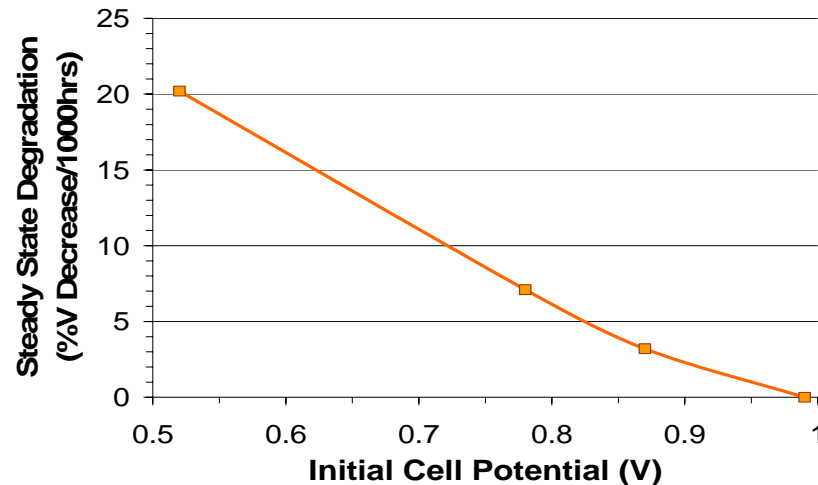
## *Substituted LSM and LSF Cathodes*

*SECA Annual Review,  
August 7-9, 2008, Pittsburgh*

*Michael Krumpelt, Brian Ingram, Terry  
Cruse*

## Sequel to the Chromium Saga

- The amount of  $\text{Cr}_2\text{O}_3$  deposited in the cathode depends on the cell potential



- Some cathodes are less affected by chromium than others
- If the deposits are formed by the electrochemical reaction



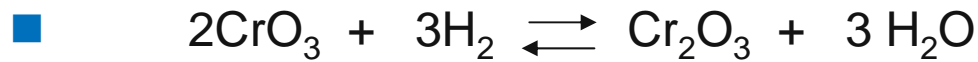
what then is the equilibrium potential?

## Thermodynamics suggest a value near 0.85 volts



$$\triangle G = + 164 \text{ KJ/mol}$$

$$\text{emf} = -0.28 \text{ V versus } \text{O}_2$$

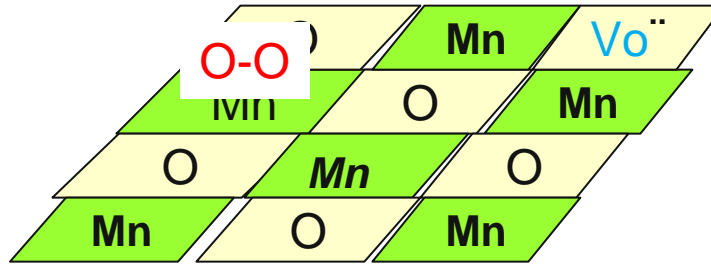


$$\triangle G = - 499 \text{ KJ/mol}$$

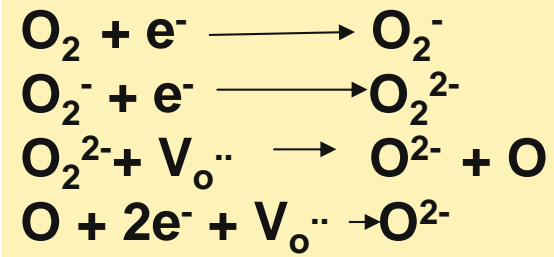
$$\text{emf} = + 0.86 \text{ V versus } \text{H}_2$$

# Oxygen Reduction Mechanism

## ■ 1 Adsorption



## ■ 2 Electron Transfer



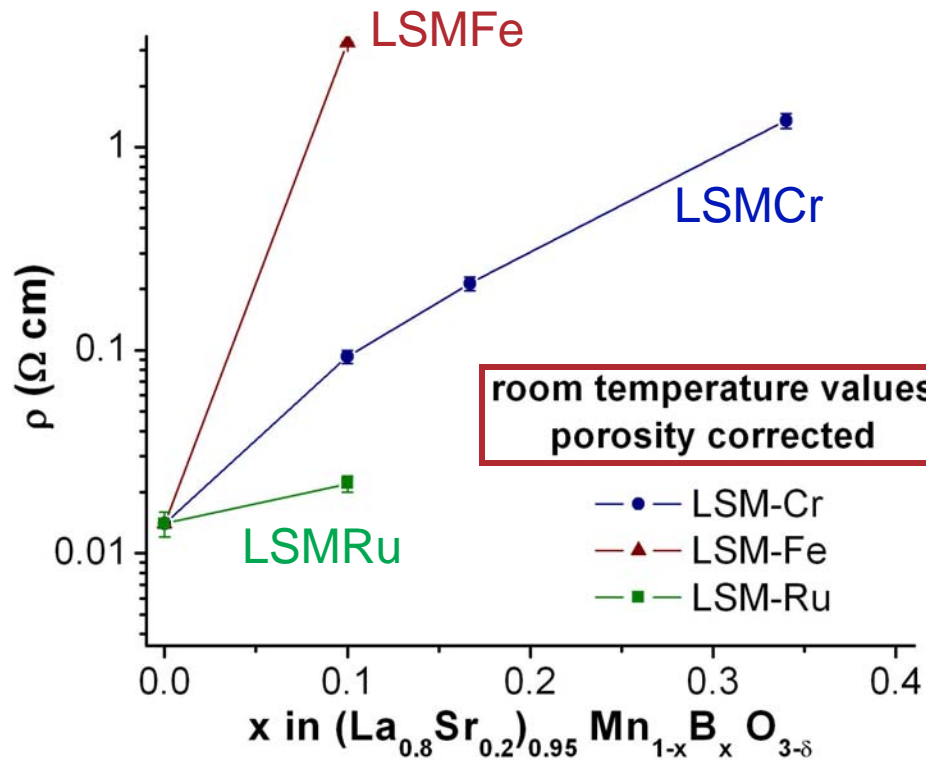
## ■ 3 Transport



## *Approach to cathode development*

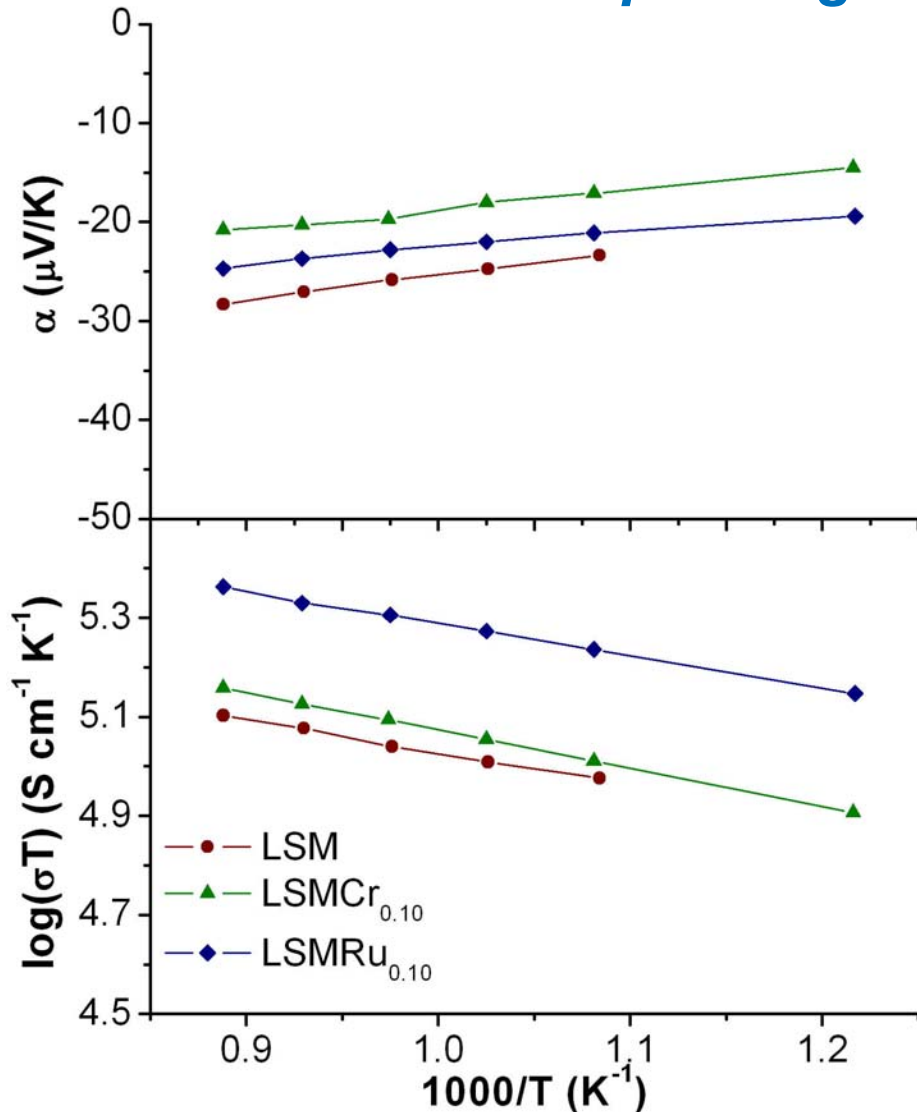
- Partially substitute “A” and/or “B” ions in LSM and LSF
- Measure
  - Area specific resistance (ASR)
  - Seebeck coefficient ( $\alpha$ )
- Characterize surface with
  - XPS/UPS
  - Multi excitation Raman spectroscopy

## Electrical resistivity of B-site substituted LSM



- At room temperature Fe and Cr serve to dilute charge carriers (Mn sites)
- Observed increase in resistivity consistent with literature

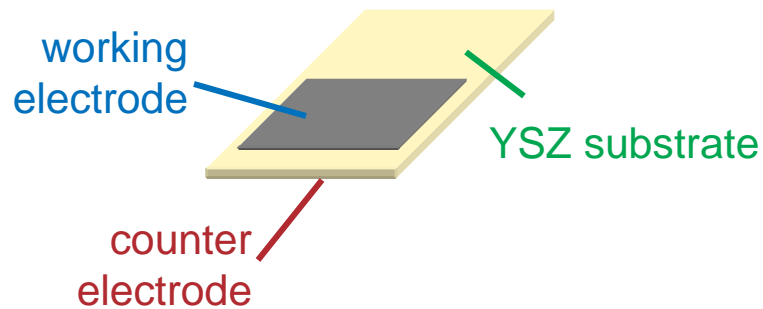
## Electrical conductivity of B-site substituted LSM at operating temperatures



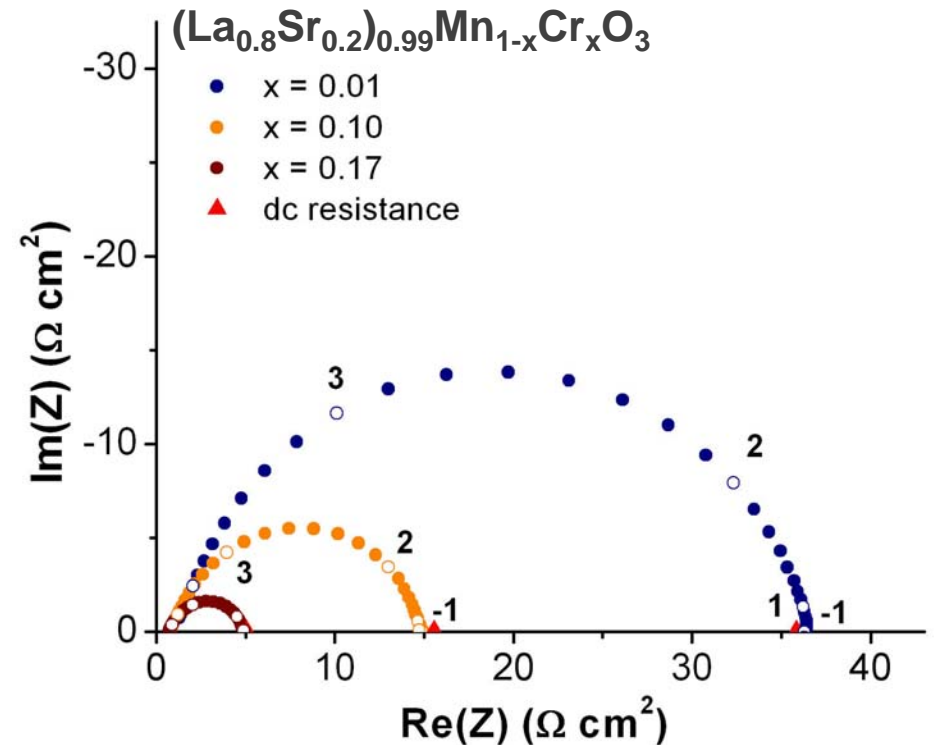
- Semiconducting behavior:  $\alpha$  decreases with increasing T
- Seebeck coefficient indicates high charge carrier concentration – little variation with B-site doping
- 40%  $\sigma$  increase with Ru
- 10%  $\sigma$  increase with Cr
- Activation energy  $\sim 0.12\text{eV}$

## ASR determination

- Symmetric 1/2 cell: perovskite electrodes screen printed



- Impedance spectra: separate electrode contribution

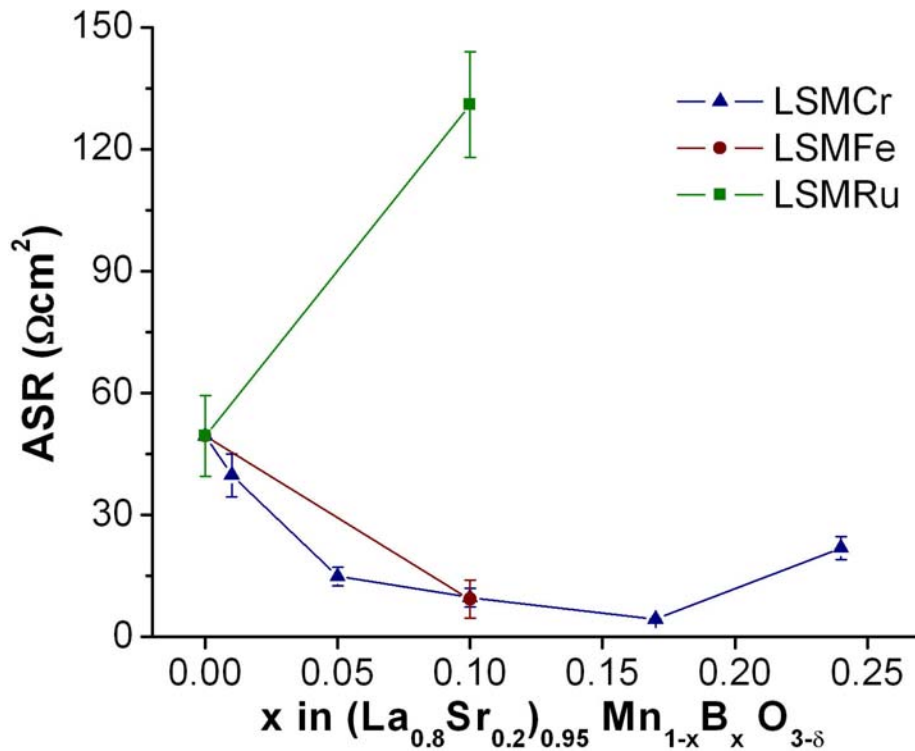


- LSMCr electrodes (single phase) at 800°C



## ASR comparison in the LSM system

B-site substituted LSM single phase electrodes at 800°C



### ■ Fe-substitution

— > 80% reduction in ASR

### ■ Cr-substitution

— > 90% reduction in ASR (17% Cr)

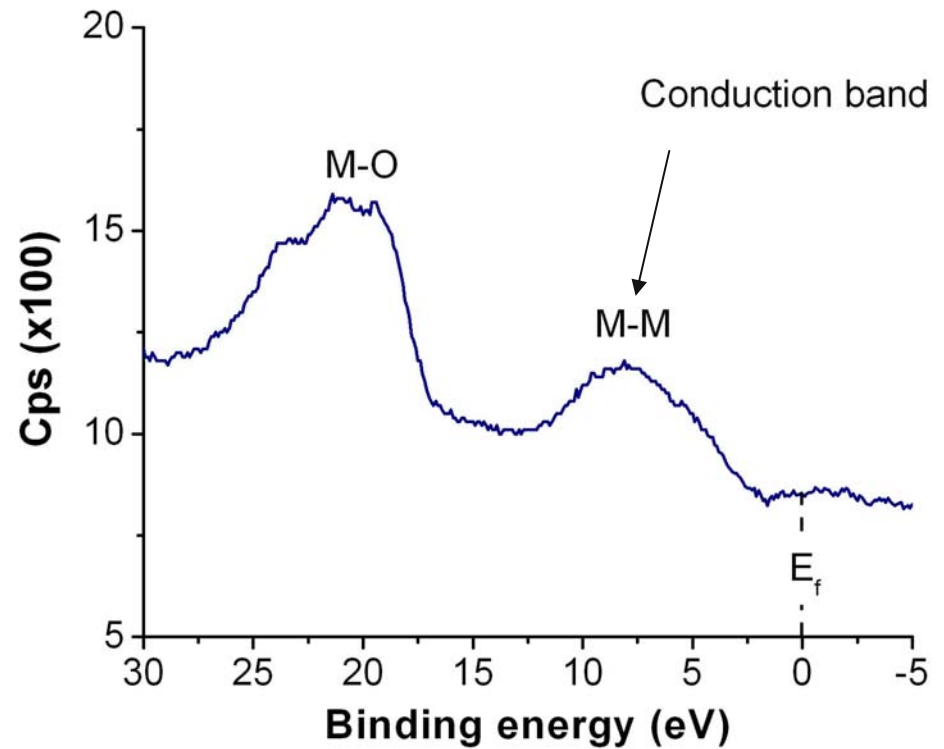
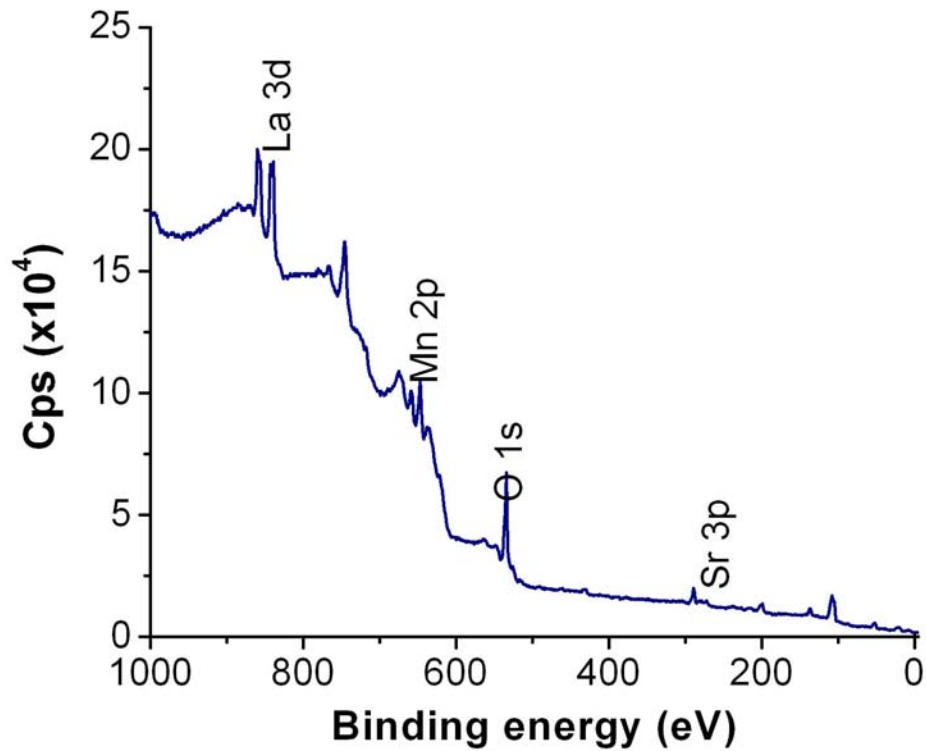
— > 80% reduction in ASR (10% Cr)

### ■ Ru-substitution

— > 60% increase in ASR

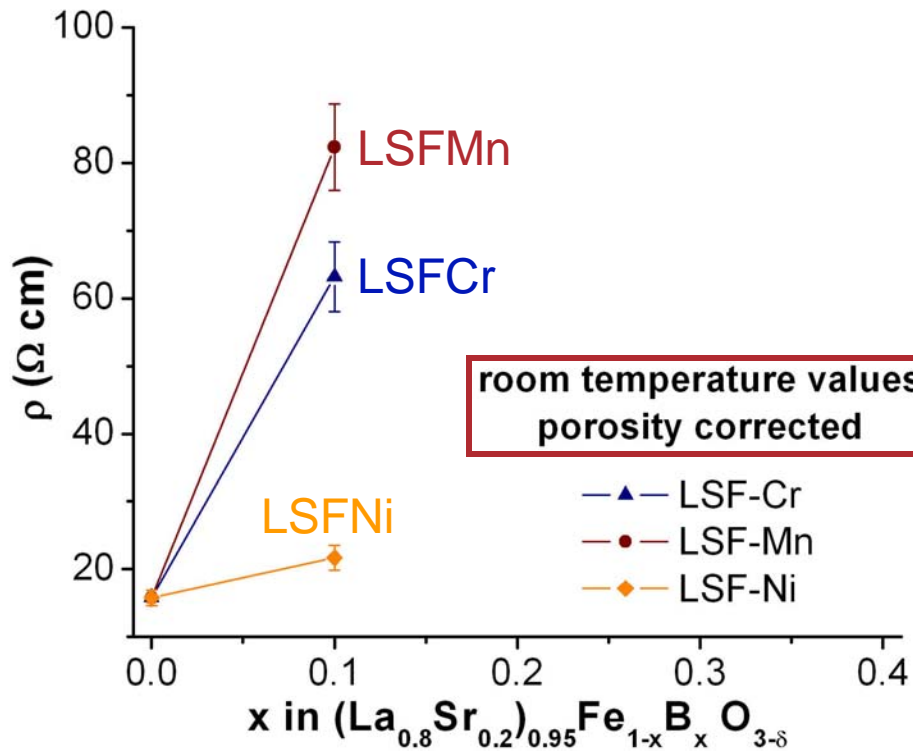
## Initial XPS results of porous LSM

- Integration of peak area indicates a surface composition of  $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.96}\text{MnO}_{3-\delta}$

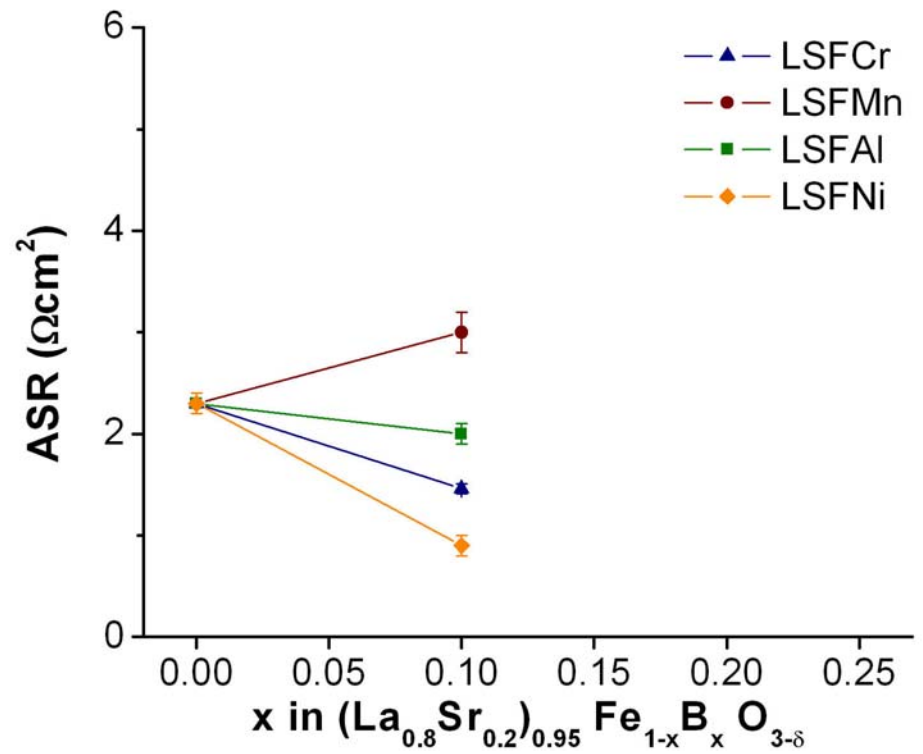


# Electrical and charge transfer resistances in ferrites

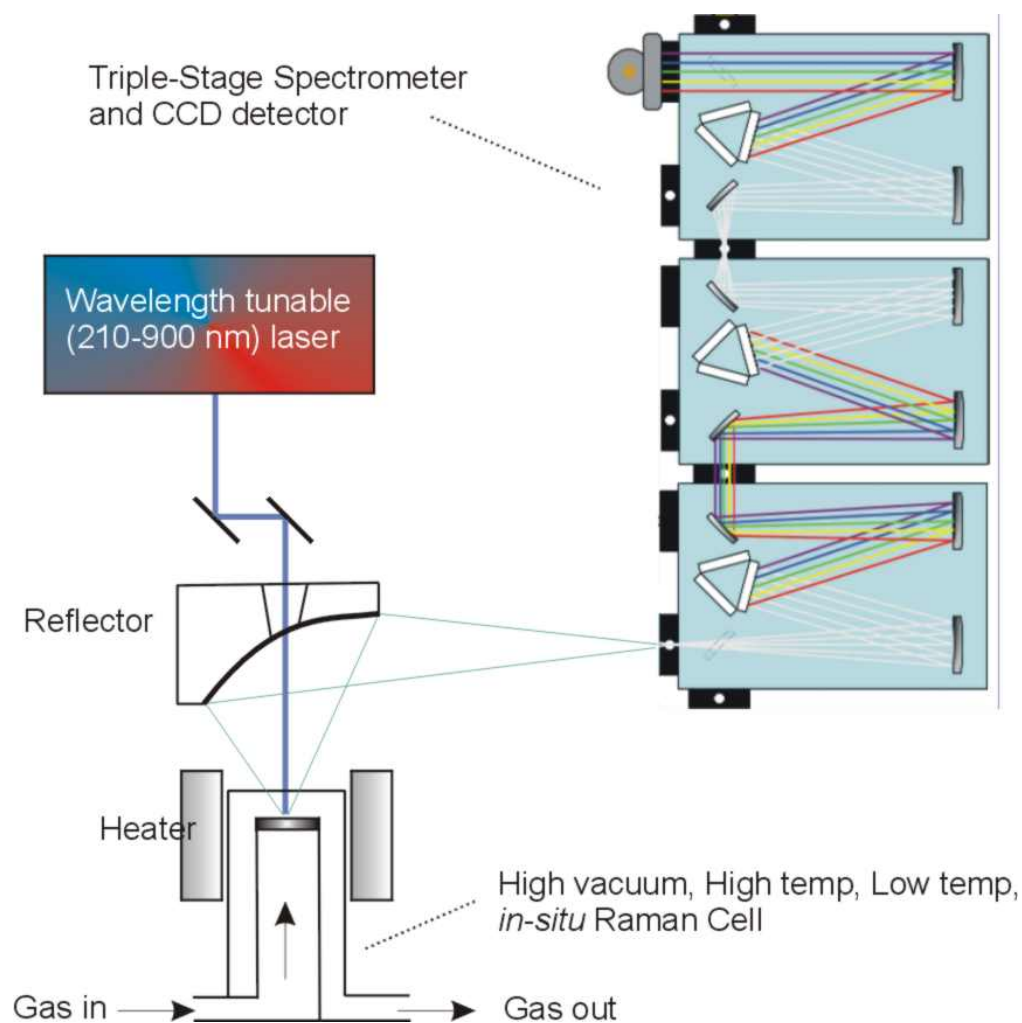
## Electrical resistance



## ASR of YSZ composites



# Multi excitation-wavelength resonance Raman spectroscopy system

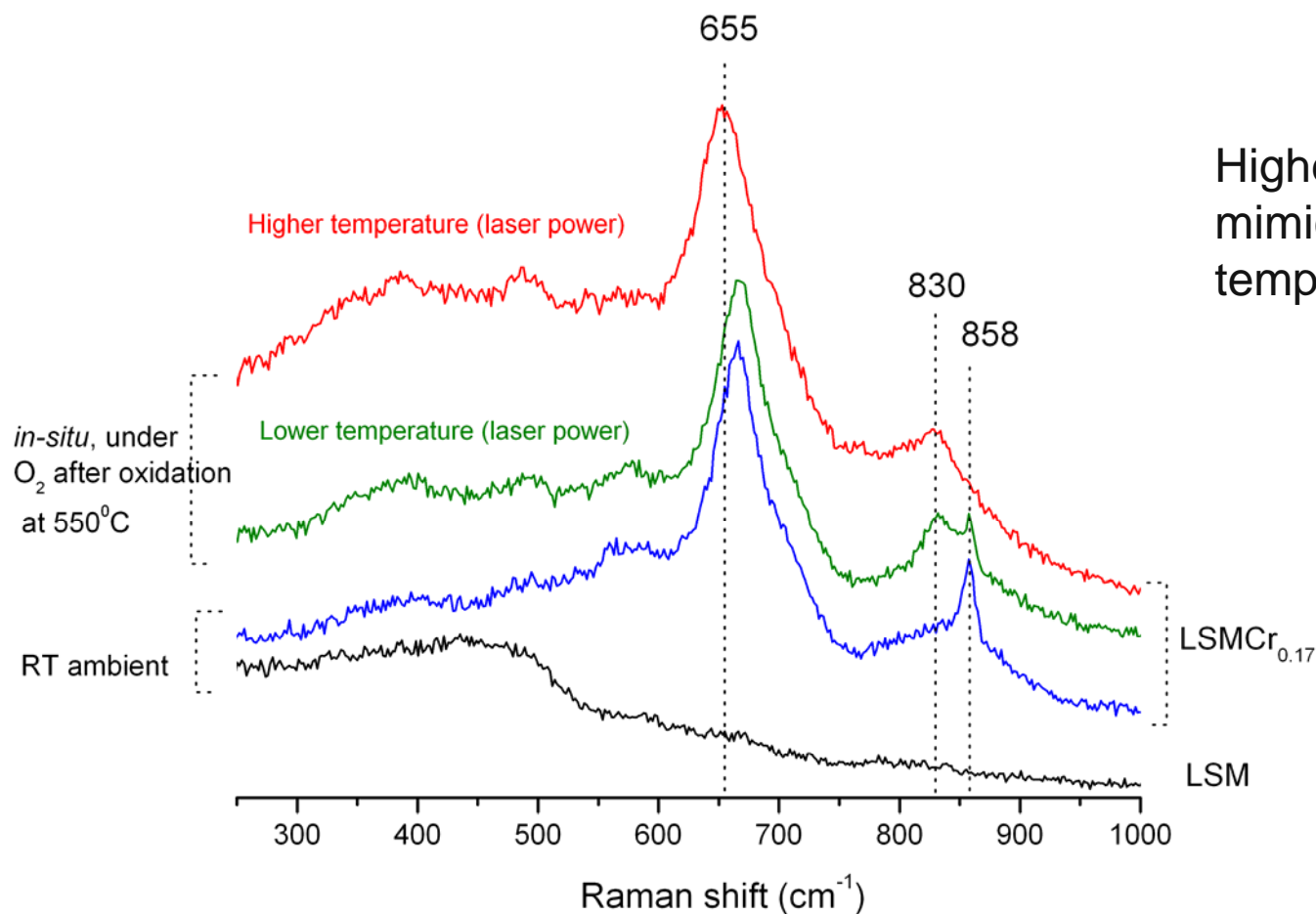


**Thanks to a wide available (deep UV to visible) excitation wavelength,**

- 1) Much higher sensitivity: some species are sensitive to UV excitation Raman, others to visible excitation Raman.
- 2) Resonance Raman capability
- 3) No fluorescence interference problem

***In addition, availability of in-situ measurements under reaction conditions at high temperatures***

## In-situ Raman spectra for LSM and LSMCr<sub>0.17</sub>



Higher laser power mimics higher temperature treatment.

- The peaks at 830 and 858 may represent peroxide and/or adsorbed oxygen attached to manganese ions.

## *Preliminary observations*

- In cathodes with good inherent ionic conductivity, good electronic conductivity can further enhance the electrochemical performance.
- In poor ionic conductors, any effects of dopants on the oxide ion vacancy concentration predominate.

## *Acknowledgements*

- This work has been conducted under the prime contract between DOE and University of Chicago LLC.
- The guidance of Briggs White and Wayne Surdoval is appreciated.