Production of Pure Hydrogen from a Source of Waste and Steam using Solid Oxide Membrane Electrolyzer

Soobhankar Pati

Kyung Joong Yoon

Srikanth Gopalan

Uday B. Pal

Materials Science & Engineering

BOSTON UNIVERSITY

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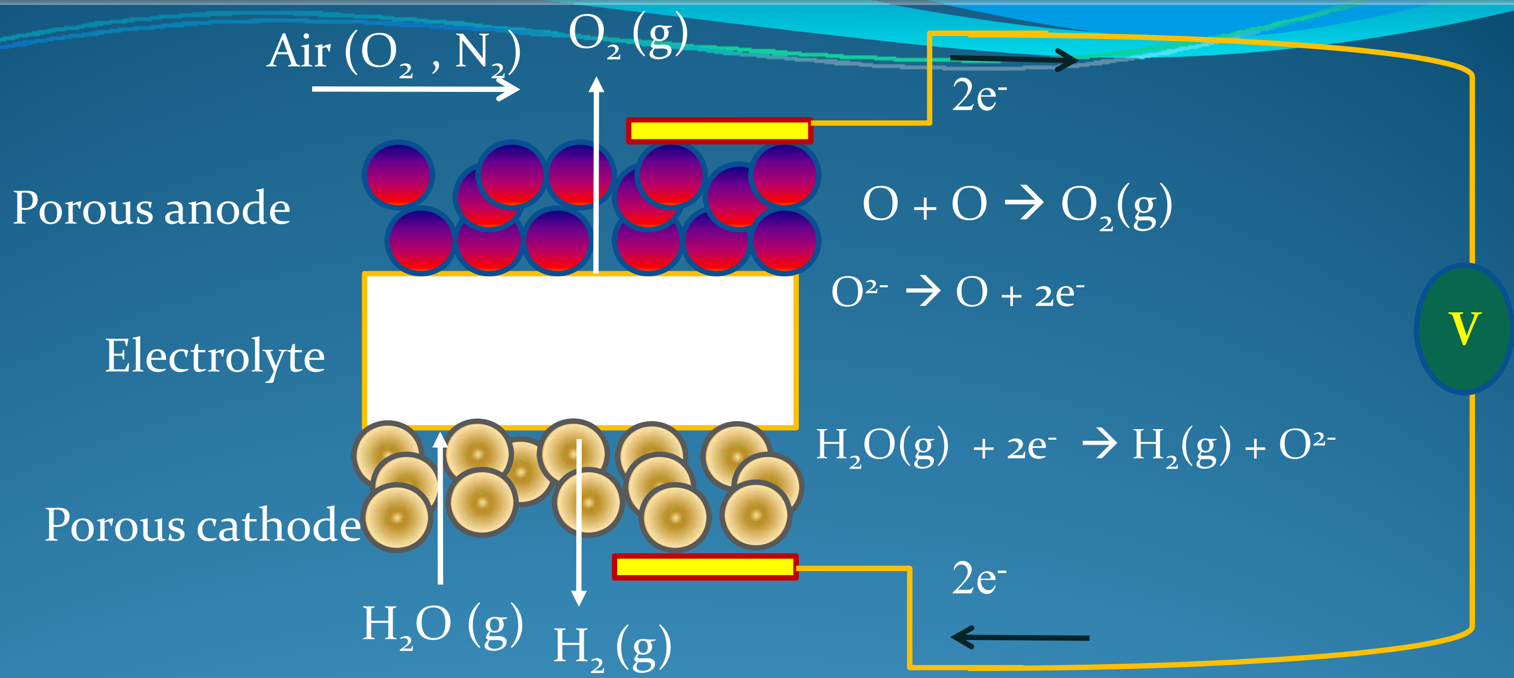
OUTLINE OF THE PRESENTATION

- Hydrogen as an energy carrier ?
- Conventional Solid Oxide Steam Electrolyzers (SOSE)
- Novel Solid Oxide Membrane (SOM) Electrolyzer
- Experiment
- Process model for the SOM Electrolyzer
- Evaluation of experimentally obtained data using the process model
- Some ongoing experiments to improve the efficiency

ELECTROLYSIS: CONVENTIONAL SOLID OXIDE STEAM ELECTROLYZER (SOSE)



Partial pressure of oxygen in air $(pO_2)_{air}$ > Partial pressure of oxygen in H_2-H_2O $(pO_2)_{H2O/H2}$

60 – 70% of the energy = THERMODYNAMIC BARRIER

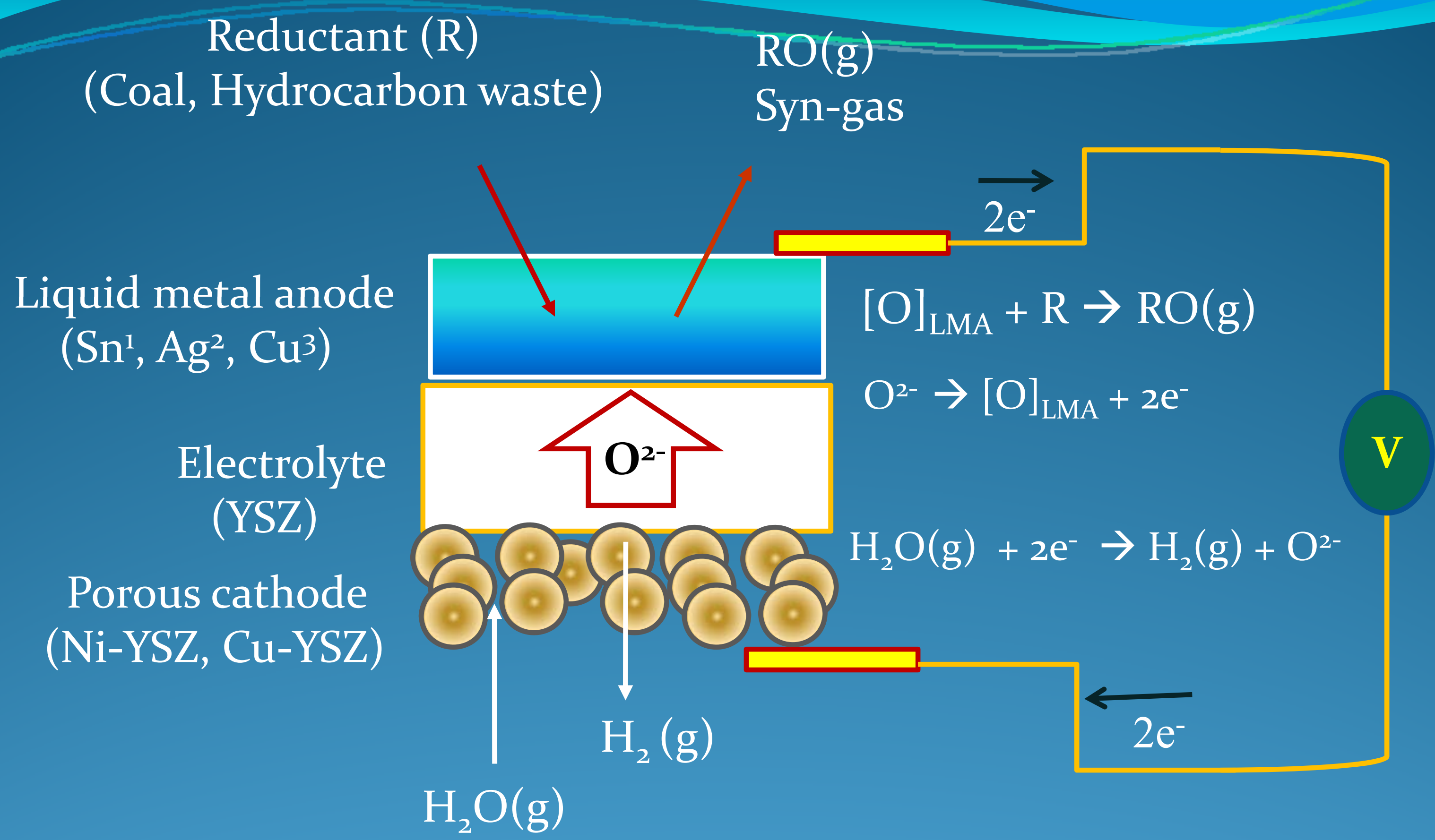
THERMODYNAMIC BARRIER → REDUCTANT AT THE ANODE

- Natural gas*
- Coal
- Hydrocarbon waste

PROBLEM: Conventional SOSE is not equipped to use reductants (waste, coal, etc.)

*J. Martinez-Frias, Ai-Quoc Pham and S. M. Aceves: *Int. J. of Hydrogen Energy*, 2003, vol.28, pp 483-90

CONFIGURATION: SOLID OXIDE MEMBRANE (SOM)ELECTROLYZER



LIQUID METAL ANODE

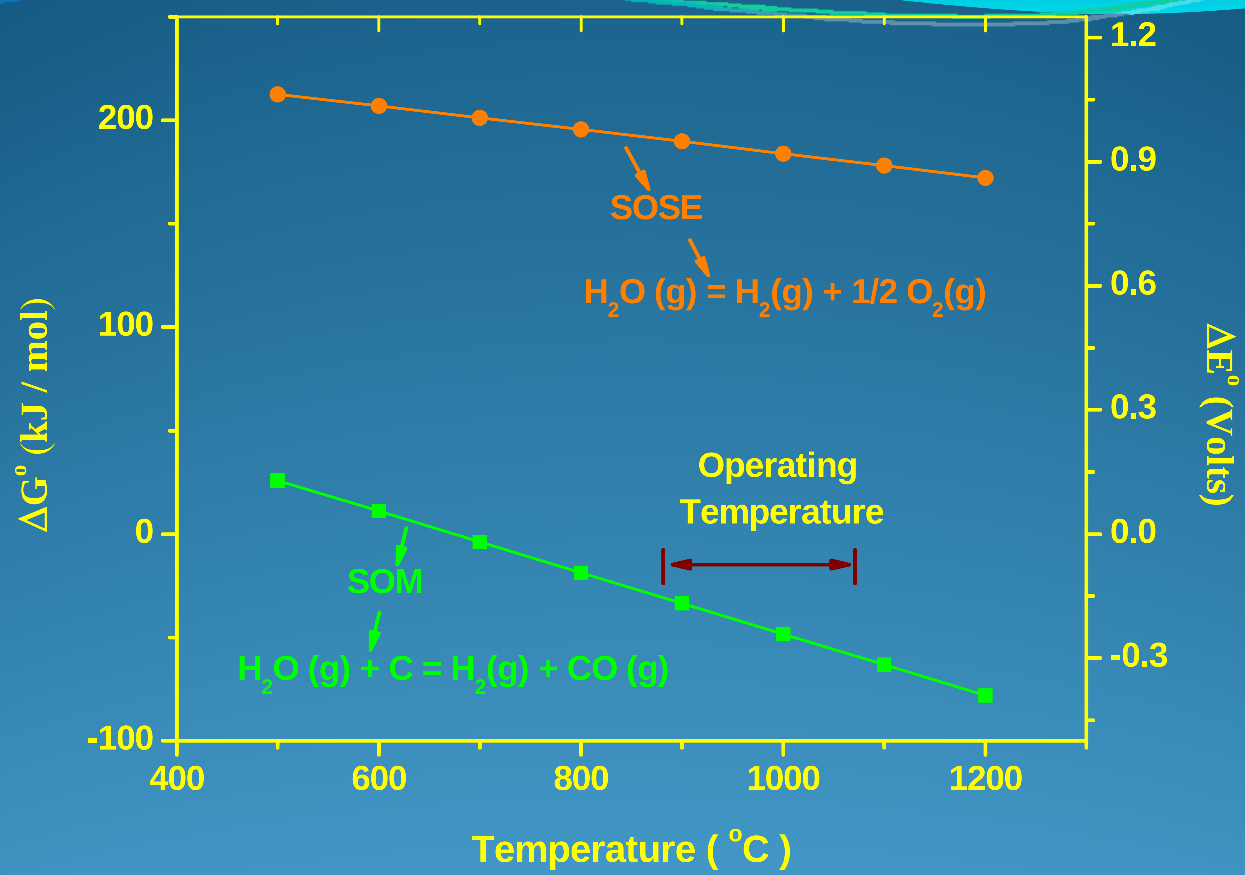
- [1, 2] Charge transfer at the YSZ/Anode interface
- [3] Reaction interface for oxidation of reductant by the $[O]_{LMA}$

[1] T. Ramanarayanan and R.A. Rapp: *Metall. Trans. B*,3, 3239 (1972)

[2] T. H. Etsell and S. N. Flengas, *Metall. Trans. B*, **2**, 2829 (1971)

[3] A. Krishnan, U. Pal and X. Lu: *Metall. Trans. B*, **36**,463 (2005)

ADVANTAGES : SOLID OXIDE MEMBRANE (SOM) ELECTROLYZER

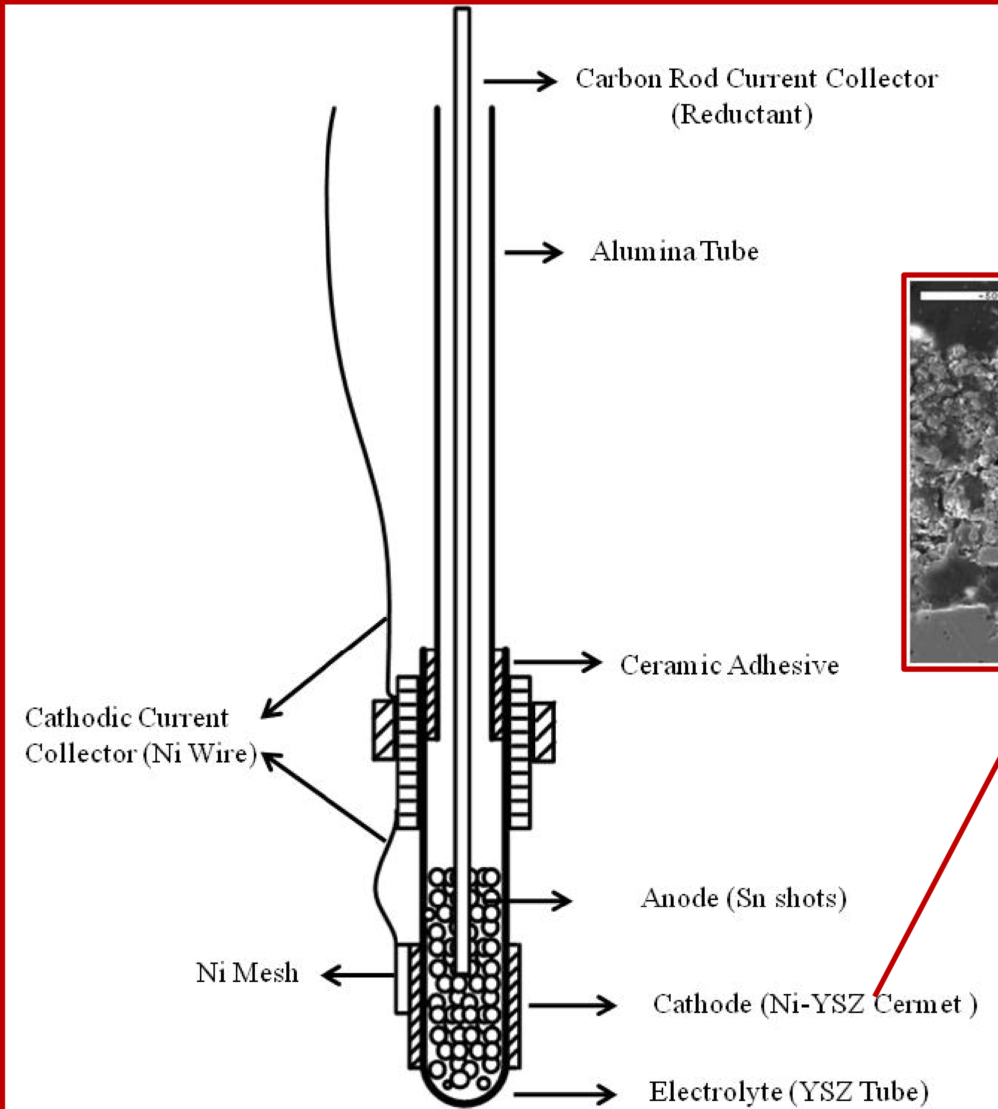


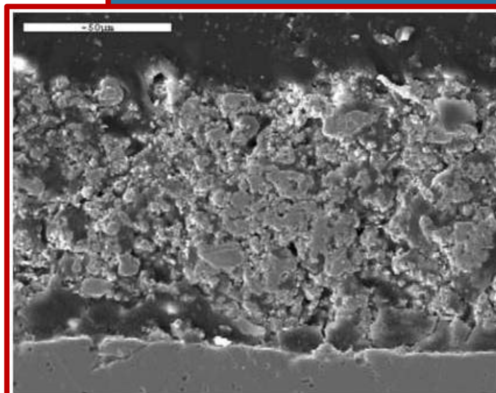
If hydrocarbon waste (HC) is used ,

$$H_2O(g) + (HC) \rightarrow H_2(g) + H_2O(g) + CO(g)$$

- Electrochemical conversion of H_2O(g) ➡ High purity H_2
- Efficient way of converting energy value in waste

EXPERIMENTAL SET UP: ELECTROCHEMICAL PERFORMANCE





Ni-YSZ cathode
~ 90 μm
~ 10% porous

YSZ electrolyte
~ 2 mm

Operating Temperature : 1000°C

ELECTROCHEMICAL CHARACTERIZATION AND PERFORMANCE

ELECTROCHEMICAL CHARACTERIZATION: OPEN CIRCUIT POTENTIAL

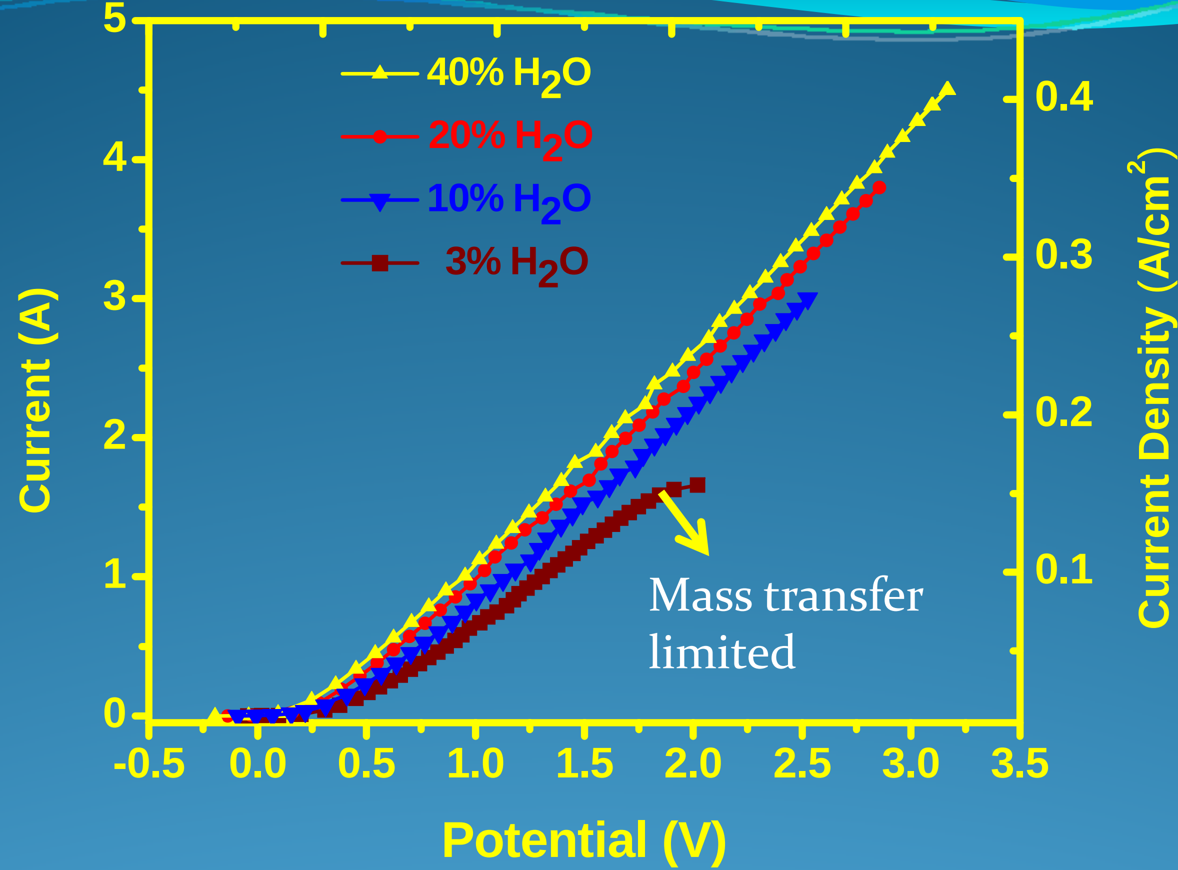
Open circuit potential (E_{eq})*,** : $E_{eq} = \frac{RT}{4F} ln\left(\frac{p^o_{O2(a)}}{p^o_{O2(c)}}\right)$

Cathodic gas composition	$p^o_{O2(a)}$ [C/CO(g) equilibrium]	Measured Values (V)
3 % H_2O - H_2	3.999×10^{-19}	-0.050
10 % H_2O - H_2		- 0.120
20 % H_2O - H_2		-0.154
40 % H_2O - H_2		- 0.207

- A negative open circuit potential (OCP) indicates the process is spontaneous
- OCP of SOSE (0.89 V) >> OCP SOM electrolyzer (-0.207 V) : 40%H_2O – H_2

* J. Martinez-Frias, Ai-Quoc Pham and S. M. Aceves: *Int. J. of Hydrogen Energy*, 2003, vol.28, pp 483-90.
** P. Soral, U. Pal, H. Larson and B. Schroeder: *Metall. Trans. B*, 1999, vol.30, pp 307-21.

ELECTROCHEMICAL CHARCTERIZATION: POTENTIODYNAMIC SCAN



- ❑ Current density increased with increase in steam content in the cathodic gas feed
- ❑ Mass transfer limitation was observed only at 3% H_2O content

  ~ Unavailability of $H_2O(g)$ at the TPBs

ELECTROCHEMICAL PERFORMANCE: POLARIZATION MODEL DEVELOPMENT

$$E_{app} = E_{eq} + \eta_{ohm} + \eta_{act} + \eta_{conc,c} + \eta_{conc,a}$$

- Open circuit potential (E_{eq}) : $E_{eq} = \frac{RT}{4F} ln\left(\frac{p^o_{O2(a)}}{p^o_{O2(c)}}\right)$
- Ohmic Polarization (η_{ohm}) $\eta_{ohm} = i\, R_{ohm}$ ⟶ R_{ohm} : YSZ , Electrodes, Contact, Lead wire
- Activation Polarization (η_{act}) : $i = i_o\, exp\left(\frac{\alpha n_e \eta_{act} F}{RT}\right) - i_o\, exp\left(-\frac{(1-\alpha) n_e \eta_{act} F}{RT}\right)$ (n_e=2, α=1/2)

$$\eta_{act} = \frac{RT}{F} ln\left[\left(\frac{i}{i_o}\right) + \sqrt{\left(\frac{i}{2i_o}\right)^2 + 1}\right]$$

⟶ (Anode + Cathode)

- Concentration Polarization (η_{conc}) : $\eta_{conc} = \eta_{conc,c} + \eta_{conc,a}$

$$\eta_{conc,c} = \frac{RT}{2F} ln\left[\frac{1 + \frac{RTt}{2FAD^{eff}_{H2-H2O} p^o_{H2(c)}} i}{1 - \frac{RTt}{2FAD^{eff}_{H2-H2O} p^o_{H2O(c)}} i}\right]$$

Cathodic concentration polarization

$$\eta_{conc,a} = \frac{RT}{2F} ln\left[1 + \frac{i}{2FAk_c C^o_{[O](Sn)}}\right]$$

Anodic concentration polarization

ELECTROCHEMICAL PERFORMANCE: CURVE FITTING

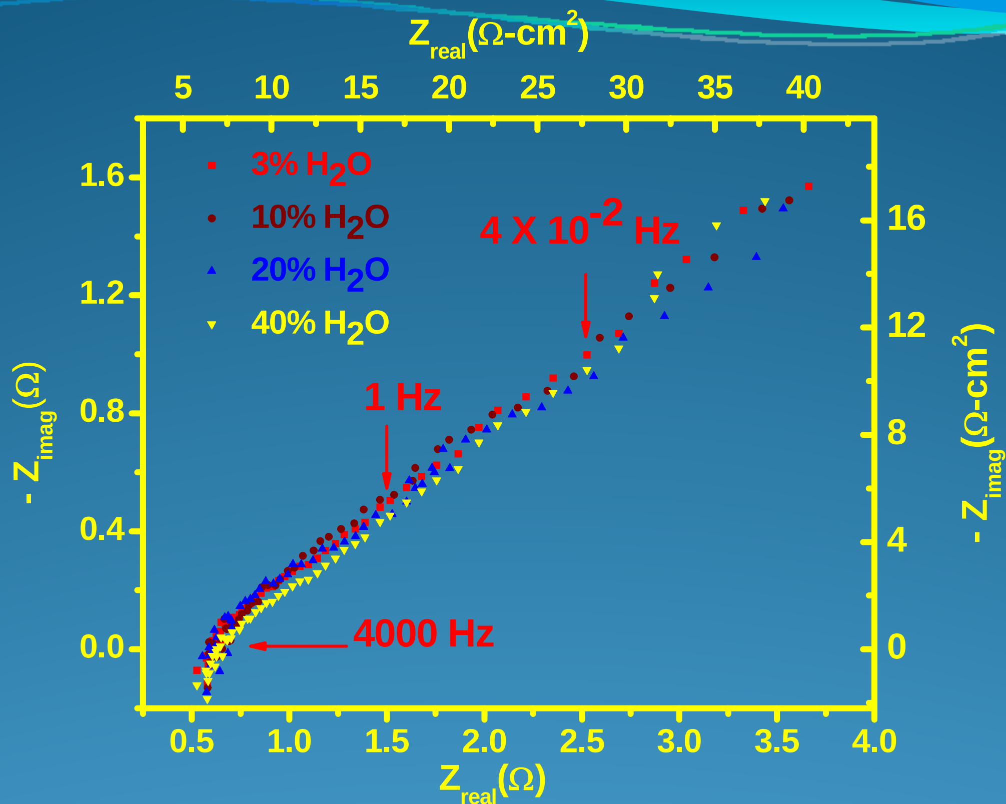
$$E_{app} = E_{eq} + i.R_{ohm} + \frac{RT}{F} ln\left[\left(\frac{i}{2i_o}\right) + \sqrt{\left(\frac{i}{2i_o}\right)^2 + 1}\right] + \frac{RT}{2F} ln\left[\frac{1 + \frac{RTt}{2FAD^{eff}_{H2-H2O}p^o_{H2(c)}} i}{1 - \frac{RTt}{2FAD^{eff}_{H2-H2O}p^o_{H2O(c)}} i}\right] + \frac{RT}{2F} ln\left[1 + \frac{i}{2Fk_c C^o_{[O](Sn)}}\right]$$

- E_{eq}: Open Circuit Potential → Measured
- $i.R_{ohm}$: Ohmic loss → Impedance spectroscopy
- Activation polarization → i_o : Fitting parameter
- Cathodic conc. polarization → D^{eff}_{H2-H2O} (Effective binary diffusivity) : Fitting parameter
- Anodic conc. polarization → $C^o_{[O](Sn)}$: Literature value*
  - k_c (Mass transfer coeff. of dissolved oxygen in the liquid tin anode) : Fitting parameter

Maximum of 2 fitting parameters used for the curve fitting ⇨ Appropriate assumption

* T. Ramanarayanan and R.A. Rapp: *Metall. Trans. B*, 1972, vol.3, pp 3239-46

ELECTROCHEMICAL PERFORMANCE: IMPEDANCE SPECTROSCOPY



- High frequency intercept : Ohmic resistance* : Independent of steam content**
- Overlap of charge transfer resistance and diffusional (Warburg) impedance at higher frequencies ***

* J.R. Macdonald : Impedance Spectroscopy, John Wiley, New York,NY,1987

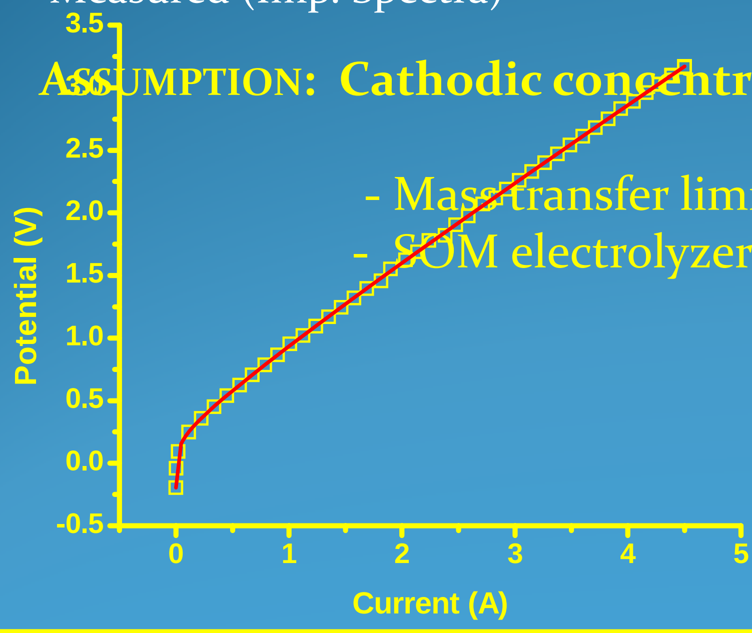
** M. A. Laguna-Bercero, S. J. Skinner and J. A. Kilner, *J. of Power Sources*, doi:10.1016/j.jpowsour.2008.12.139,(2009)

*** S. Britten and U. Pal, *Metall. and Mat. Transactions B*, **31**, 733 (2000)

ELECTROCHEMICAL PERFORMANCE: CURVE FITTING (40% H_2O in cathodic gas)

$$E_{app} = E_{eq} + i.R_{ohm} + \frac{RT}{F} ln\left[\left(\frac{i}{2i_o}\right) + \sqrt{\left(\frac{i}{2i_o}\right)^2 + 1}\right] + \frac{RT}{2F} ln\left[\frac{1 + \frac{RTt}{2FAD^{eff}_{H2-H2O}p^o_{H2(c)}} i}{1 - \frac{RTt}{2FAD^{eff}_{H2-H2O}p^o_{H2O(c)}} i}\right] + \frac{RT}{2F} ln\left[1 + \frac{i}{2Fk_cC^o_{[O](Sn)}}\right]$$

- Open Circuit Potential → Measured
- Ohmic loss → Measured (Imp. Spectra)
- Activation polarization → i_o: Fitting parameter
- Cathodic conc. polarization → Insignificant
- Anodic conc. polarization → k_c: Fitting parameter



ASSUMPTION: Cathodic concentration polarization ($\eta_{conc, c}$) is negligible*

- Mass transfer limitation not observed
- SOM electrolyzer is electrolyte supported with thin Ni- YSZ cathode

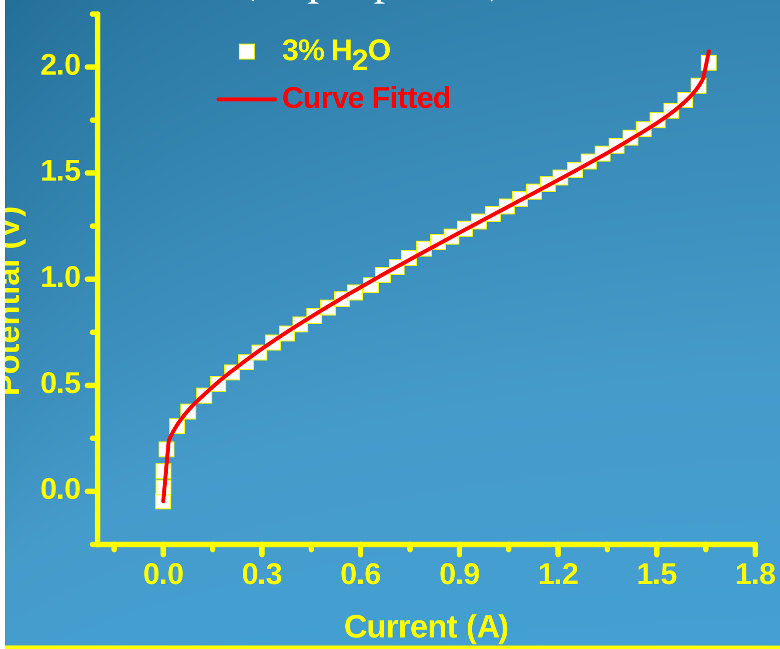
Fitting parameters	Curve fitting results
Exchange current (i_o)	1.00A
Mass transfer coefficient (k_c)	0.00056 cm/sec

* M. Ni, M.K.H. Leung and D.Y.C. Leung: *Int. J of Hyd. Energy*, 2007, vol. 32, pp 2305-13

ELECTROCHEMICAL PERFORMANCE: CURVE FITTING (3% H_2O in cathodic gas)

$$E_{app} = E_{eq} + i.R_{ohm} + \frac{RT}{F} ln\left[\left(\frac{i}{2i_o}\right) + \sqrt{\left(\frac{i}{2i_o}\right)^2 + 1}\right] + \frac{RT}{2F} ln\left[\frac{1 + \frac{RTt}{2FAD^{eff}_{H2-H2O}p^o_{H2(c)}} i}{1 - \frac{RTt}{2FAD^{eff}_{H2-H2O}p^o_{H2O(c)}} i}\right] + \frac{RT}{2F} ln\left[1 + \frac{i}{2Fk_c C^o_{[O](Sn)}}\right]$$

- Open Circuit Potential → Measured
- Ohmic loss → Measured (Imp. Spectra)
- Activation polarization → i_o : Fitting parameter
- Cathodic conc. polarization → D^{eff}_{H2-H2O} : Fitting parameter
- Anodic conc. polarization → k_c : Independent of cathodic gas comp.* → k_c : 40 % curve fitting (0.00056 cm/sec)



Fitting parameters	Curve fitting results
Exchange current (i_o)	0.12 A
Effective Binary Diffusivity ($D^{eff}_{H_2\text{-}H_2O}$)	0.025 cm^2/sec

*S. Yuan, K.C. Chou, U. Pal: *J. Elec. Soc.*,1994, vol. 141, pp. 467-74

ELECTROCHEMICAL PERFORMANCE: CURVE FITTING (10 % and 20 % H_2O)

$$E_{app} = E_{eq} + i.R_{ohm} + \frac{RT}{F} ln\left[\left(\frac{i}{2i_o}\right) + \sqrt{\left(\frac{i}{2i_o}\right)^2 + 1}\right] + \frac{RT}{2F} ln\left[\frac{1+\frac{RTt}{2FAD^{eff}_{H2-H2O}p^o_{H2(c)}}i}{1-\frac{RTt}{2FAD^{eff}_{H2-H2O}p^o_{H2O(c)}}i}\right] + \frac{RT}{2F} ln\left[1+\frac{i}{2Fk_cC^o_{[O](Sn)}}\right]$$

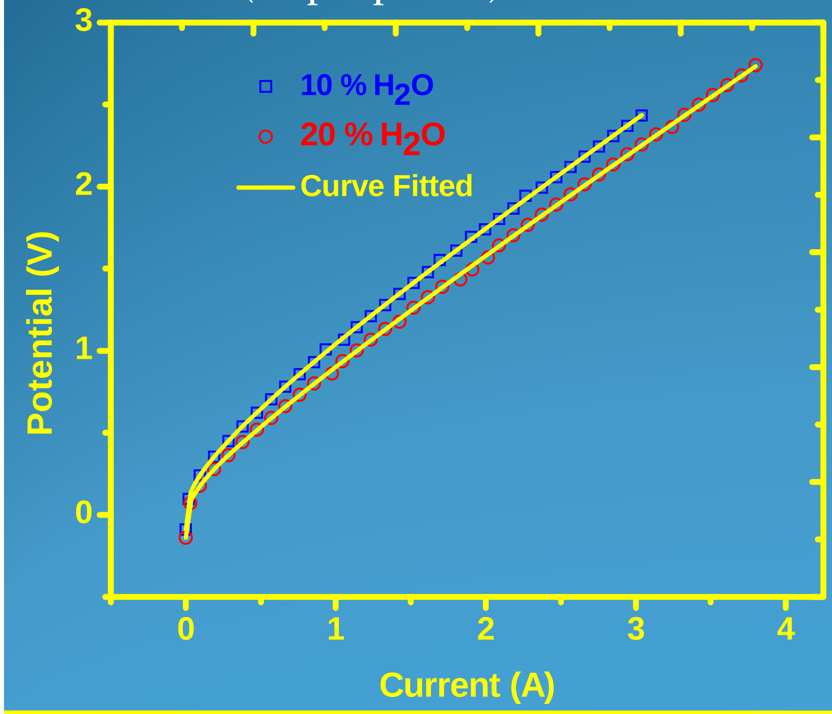
Open Circuit Potential → Measured

Ohmic loss → Measured (Imp. Spectra)

Activation polarization → i_o : Fitting parameter

Cathodic conc. polarization → D^{eff}_{H2-H2O} :Independent of cathodic gas comp.* → D^{eff}_{H2-H2O} :3% curve fitting (0.025 cm²/sec)

Anodic conc. polarization → k_c : 40 % curve fitting (0.00056 cm/sec



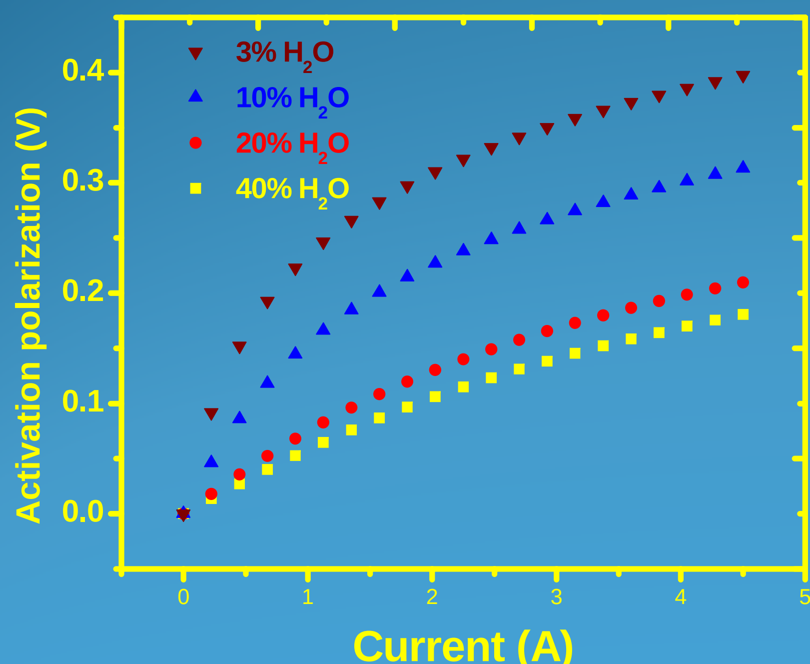
Cathode gas composition	Exchange current (i_0)
10 % H_2O – H_2	0.26 A
20 % H_2O – H_2	0.68 A

R. B. Bird, W. E. Stewart and E. N. Lightfoot: *Transport Phenomena*, 2nd ed., John Wiley & Sons, New York, 2002

ELECTROCHEMICAL PERFORMANCE : ACTIVATION POLARIZATION

Cathode gas composition	Exchange current (i_0)
3 % $H_2O - H_2$	0.12 A
10 % $H_2O - H_2$	0.26 A
20 % $H_2O - H_2$	0.68 A
40 % $H_2O - H_2$	1.00 A

$$\eta_{act} = \frac{RT}{F} ln\left[\left(\frac{i}{2i_o}\right) + \sqrt{\left(\frac{i}{2i_o}\right)^2 + 1}\right]$$



H_2O content ⇧

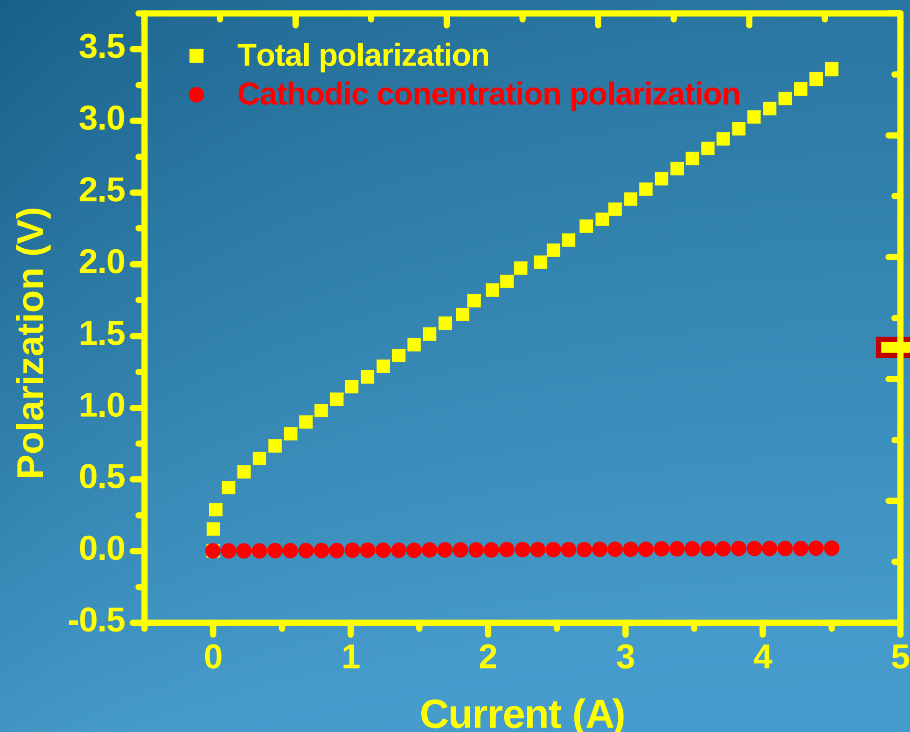
=> Surface coverage of H_2O (g) at TPB's ⇧

Provides additional sites for the charge transfer reaction

ELECTRO. PERFORM.: CATHODIC CONC. POLARIZATION (40% H_2O)

D^{eff}_{H2-H2O} is composition independent

$$\eta_{conc,c} = \frac{RT}{2F} ln\left[\frac{1 + \frac{RTt}{2FAD^{eff}_{H2-H2O}p^{o}_{H2(c)}} i}{1 - \frac{RTt}{2FAD^{eff}_{H2-H2O}p^{o}_{H2O(c)}} i}\right]$$



Cathodic concentration polarization

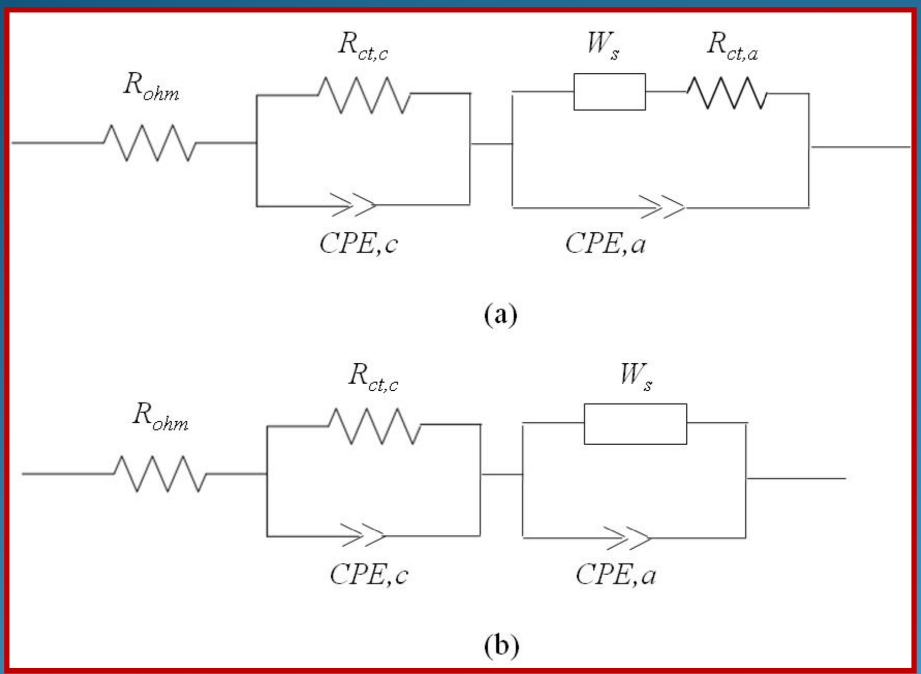
1% of the total overpotential

Cathodic concentration polarization is insignificant at 40% H_2O

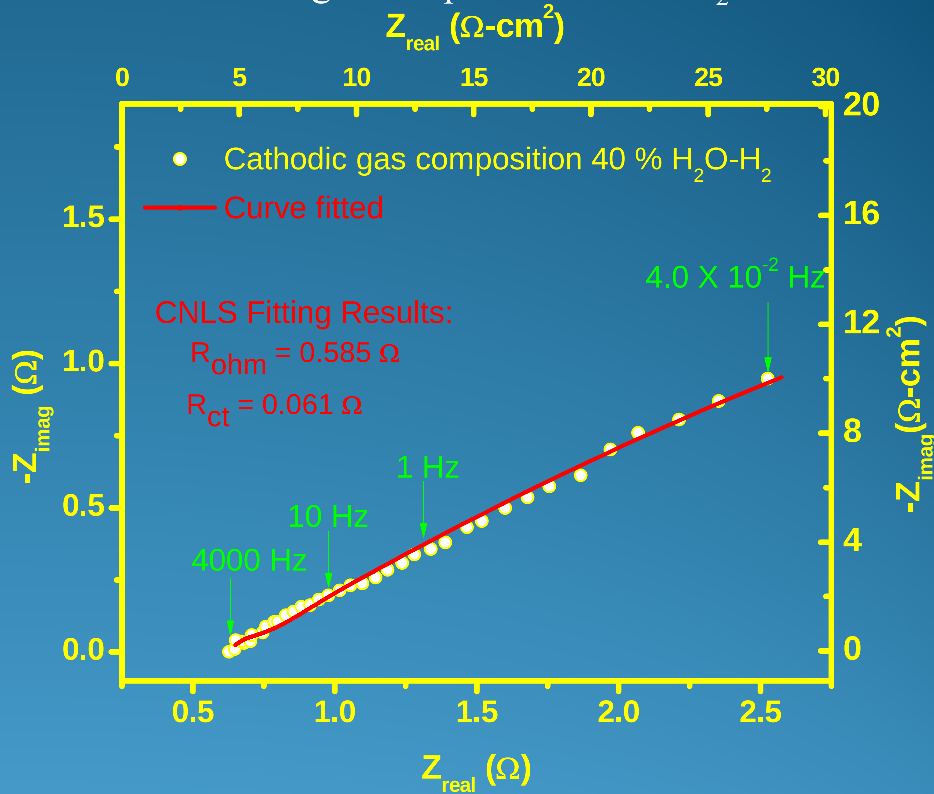
: Consistent with our initial assumption

ELECTRO. PERFORM.: IMPEDANCE SPECTROSCOPY IN SUPPORT OF POLARIZATION MODELING

Equivalent circuit describing the SOM electrolyzer



Cathodic gas composition :40 % H_2O



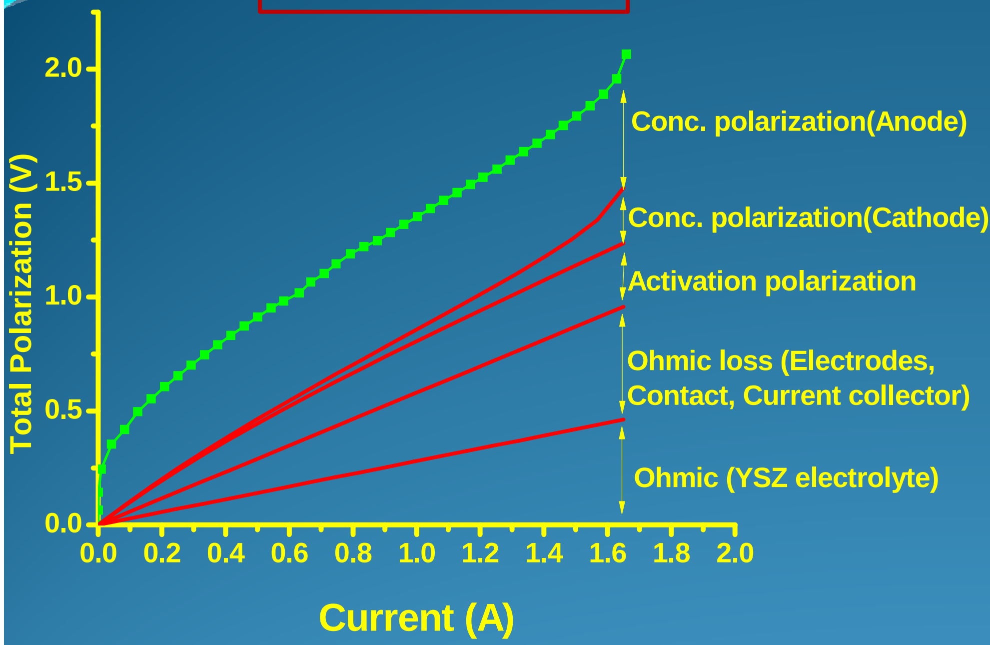
At small activation polarization,

$$R_{ct,c} = \frac{RT}{nFi_o}$$

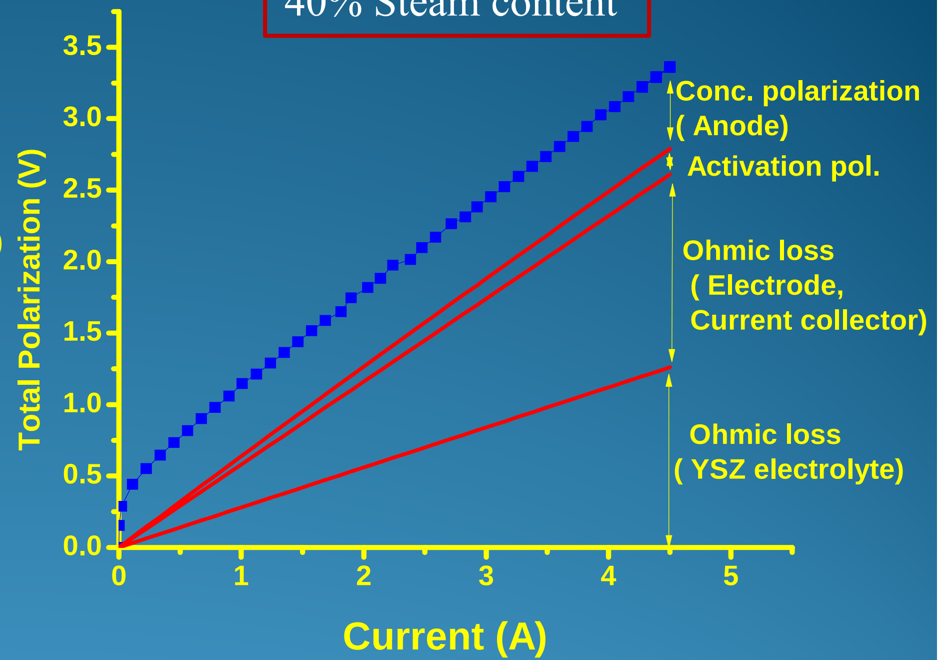
	Polarization modeling	CNLS Fitting
Ohmic Loss (R_{ohm})	0.58Ω	0.585Ω
Charge transfer resistance ($R_{ct,c}$)	0.054Ω	0.061 Ω

ELECTROCHEMICAL PERFORMANCE: VARIOUS POLARIZATION LOSSES

3% Steam content



40% Steam content



- At 3% H_2O the ohmic part ≈ Overpotential due to electrode processes

- At 40% H_2O ohmic resistance is ~ 80.5% of the total polarization
  Electrodes, Contacts, Current collector ~ 52 % of the ohmic loss
  YSZ electrolyte resistance ~ 48 % of the ohmic loss

Ohmic loss due to the dominates the performance loss:

- Molybdenum current collectors on the anodic side
- SOM electrolyzer design (Electrode supported)

SUMMARY

- The potential of hydrogen production from steam using a solid oxide membrane electrolyzer with a liquid anode was demonstrated.
- Thermodynamic barrier was lowered using a reductant in the liquid metal anode.
- Using an electrolyte supported design and applying only 2.0 V , a current density of 0.5 A/cm^2 was achieved.
- Polarization modeling results thus showed that the performance is rate-controlled by the ohmic loss.
- Experimental study and modeling will form the basis for redesigning the SOM electrolyzer to improve its efficiency and for investigating various types of waste feed.