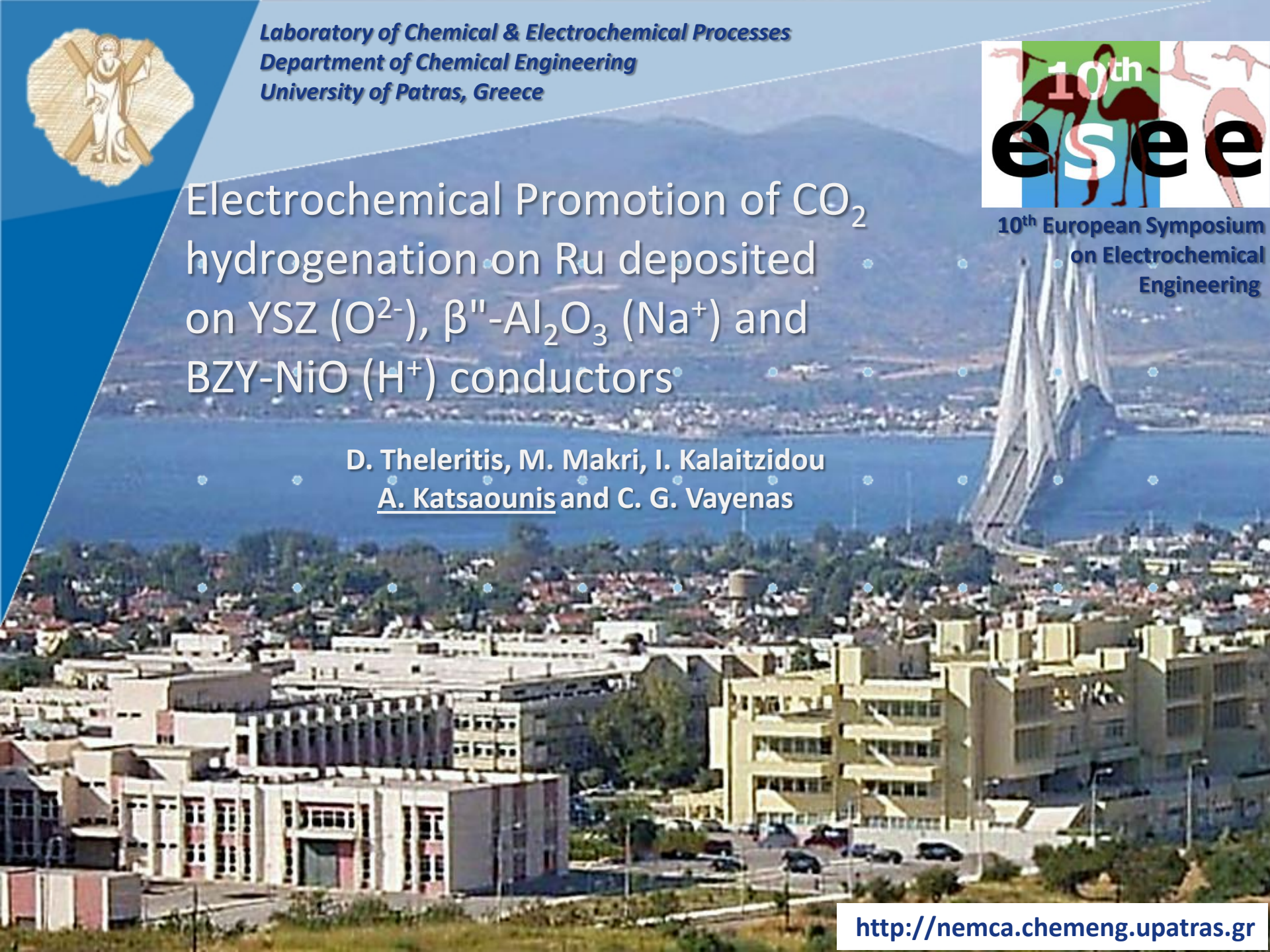
Laboratory of Chemical & Electrochemical Processes
Department of Chemical Engineering
University of Patras, Greece

10th esee

10th European Symposium on Electrochemical Engineering

Electrochemical Promotion of CO_2 hydrogenation on Ru deposited on YSZ (O^{2-}), β"-Al_2O_3 (Na^+) and BZY-NiO (H^+) conductors

D. Theleritis, M. Makri, I. Kalaitzidou
A. Katsaounis and C. G. Vayenas



Outline

Introduction

- CO_2 Hydrogenation
- Electrochemical Promotion of Catalysis

Experimental Procedure

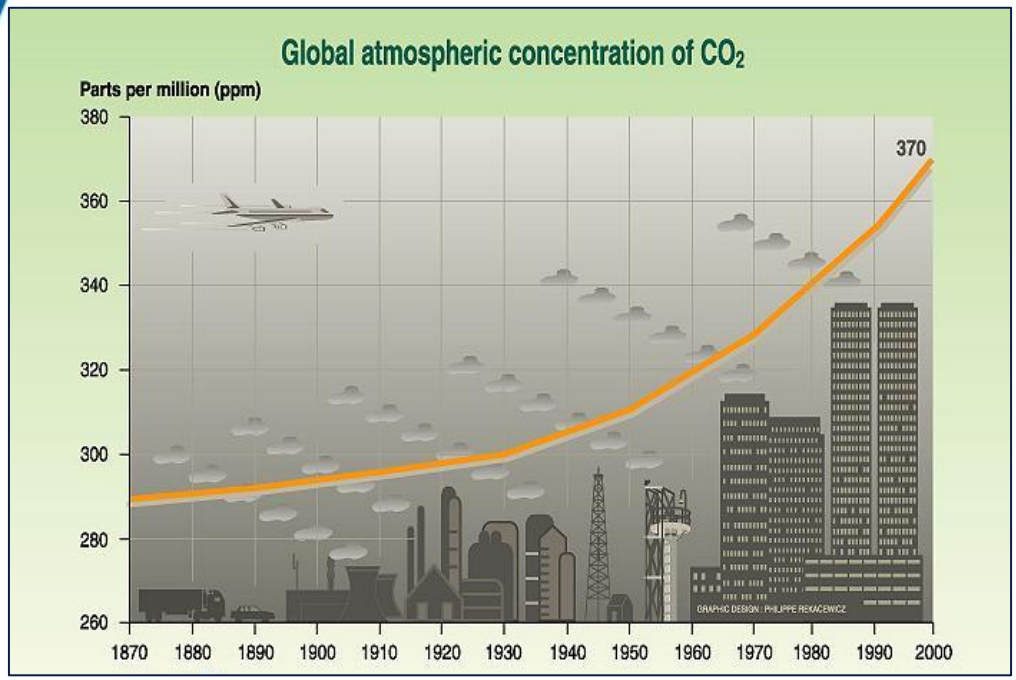
- preparation and characterization of the catalysts
- Experimental setup - Reactor

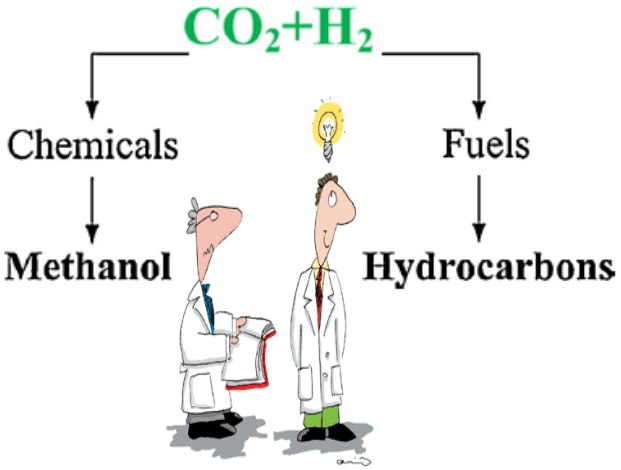
Electrochemical Promotion of CO_2 Hydrogenation

- Ru/BZY, Ru/YSZ, Ru/β''-Al_2O_3 electrochemical cell
- Comparative Results

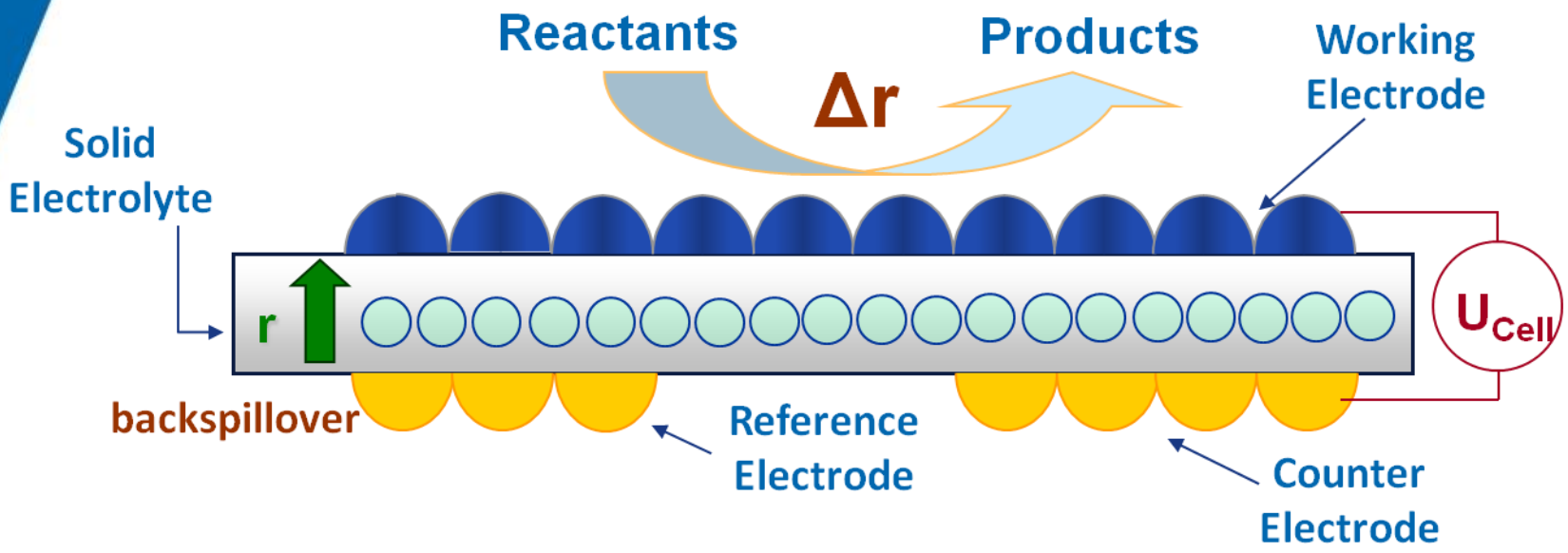
Discussion - Conclusions

CO_2 Hydrogenation



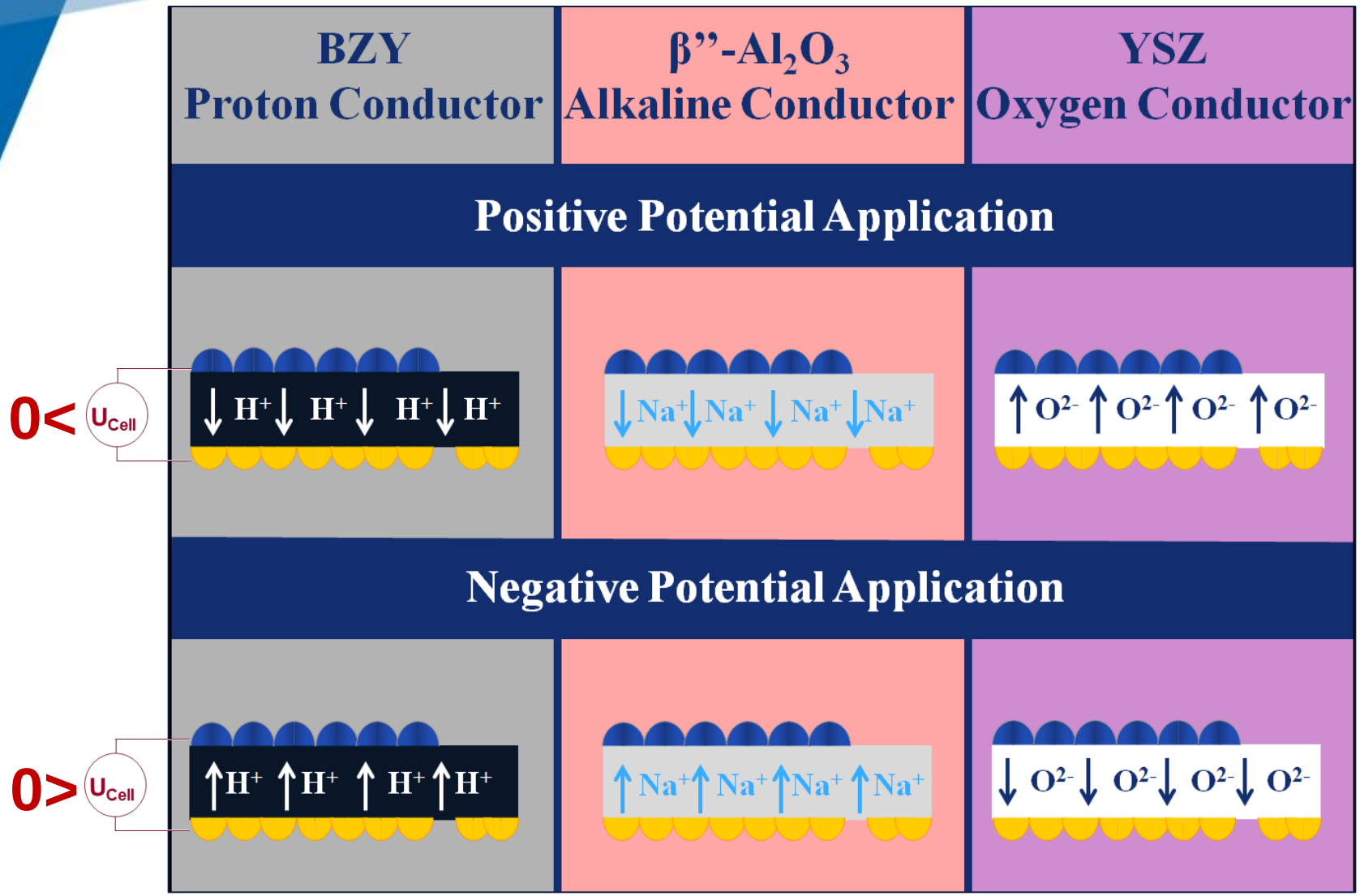


Electrochemical Promotion of Catalysis EPOC



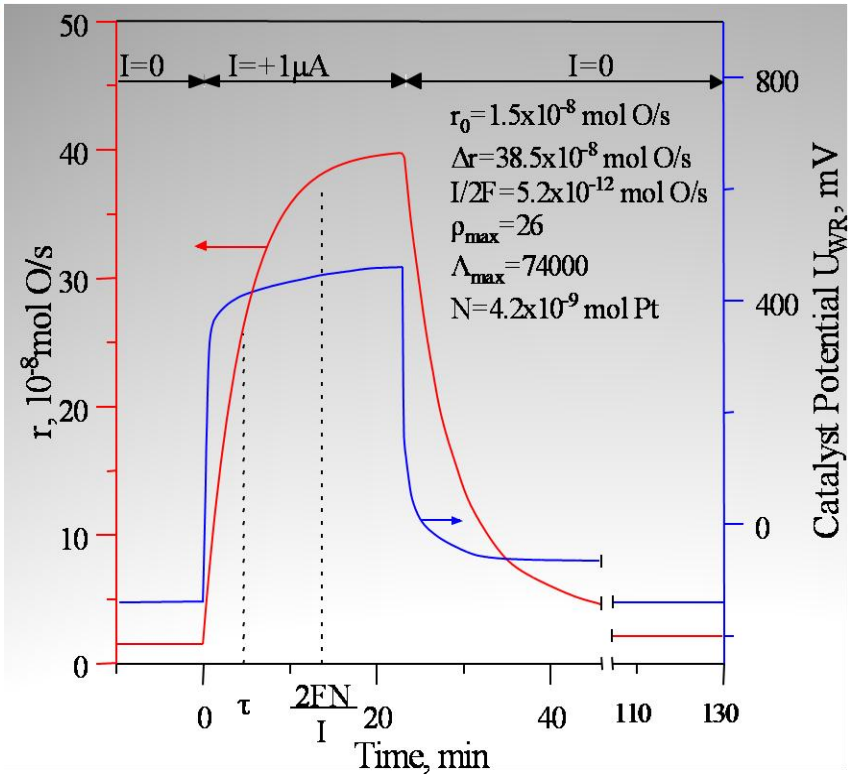
M. Stoukides and C.G. Vayenas, *J. Catal.*, 70 (1981) 137.

Electrochemical Promotion of Catalysis EPOC



Electrochemical Promotion of Catalysis EPOC

C_2H_4 oxidation on Pt



Faradaic Efficiency

$$\Lambda = \frac{\Delta r}{I/nF}$$

Δr ⟶ $r - r_0$

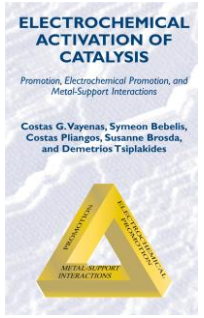
r, r_0 ⟶ rate of production / consumption(g-mol/s) under closed and open (I=0) circuit

I/nF ⟶ ion transfer rate

Rate Enhancement Ratio

$$\rho = \frac{r}{r_0}$$

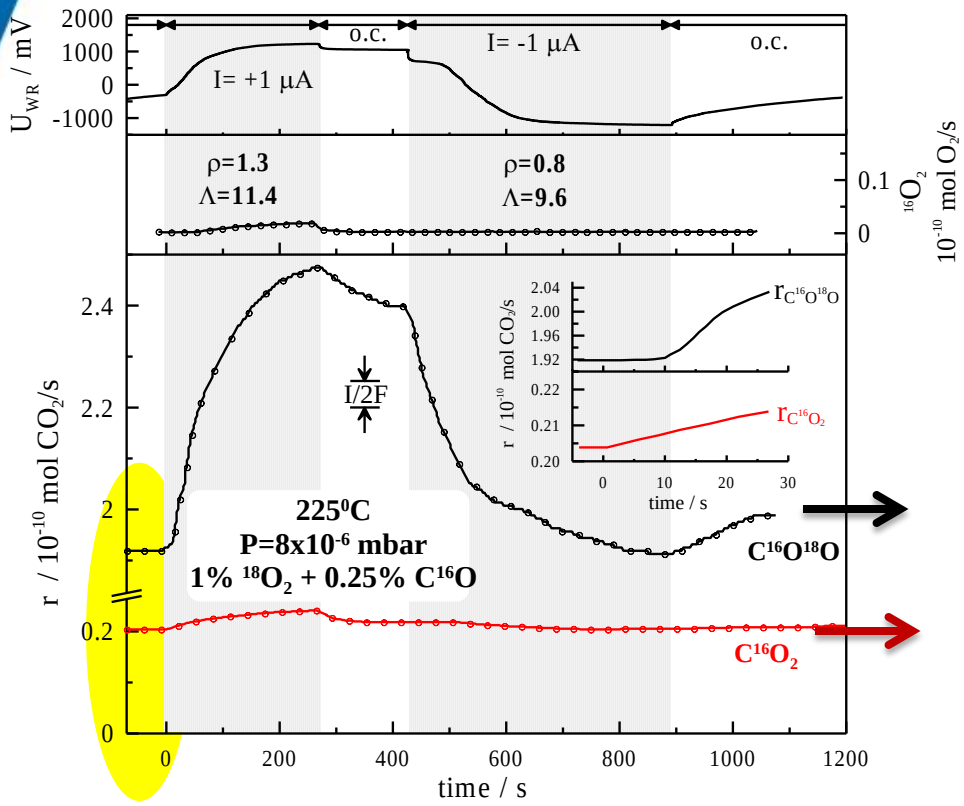
| Λ | > 1 → **Non – Faradaic Electrochemical Modification of Catalytic Activity (NEMCA)**



"Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions"
C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsiplakides, Kluwer Academic/Plenum Publishers (2001).

Electrochemical Promotion of Catalysis EPOC

CO oxidation with labeled oxygen $^{18}O_2$ on Pt



open circuit catalytic reaction

Faradaic Efficiency

$$\Lambda = \frac{\Delta r}{I/nF}$$

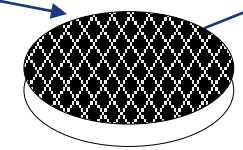
CO + ^{18}O → $C^{16}O^{18}O$ (mass 46)

CO + ^{16}O → $C^{16}O^{16}O$ (mass 44)

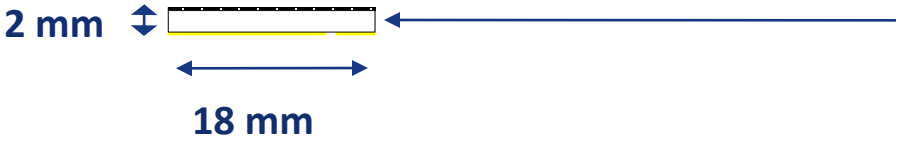
A. Katsaounis, Z. Nikopoulou, X.E. Verykios, C.G. Vayenas, *J. Catal.* 222 (2004) 192 and J. Catalysis 226 (2004) 197.

Preparation of electrochemical Cells

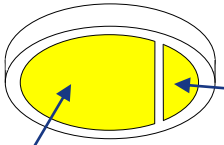
Catalyst (Ru)
Working electrode



- **Wet impregnation of $RuCl_3$ solution (150mM)**
- **Calcination at 650°C for 1 h**



Solid electrolyte



Reference electrode Au

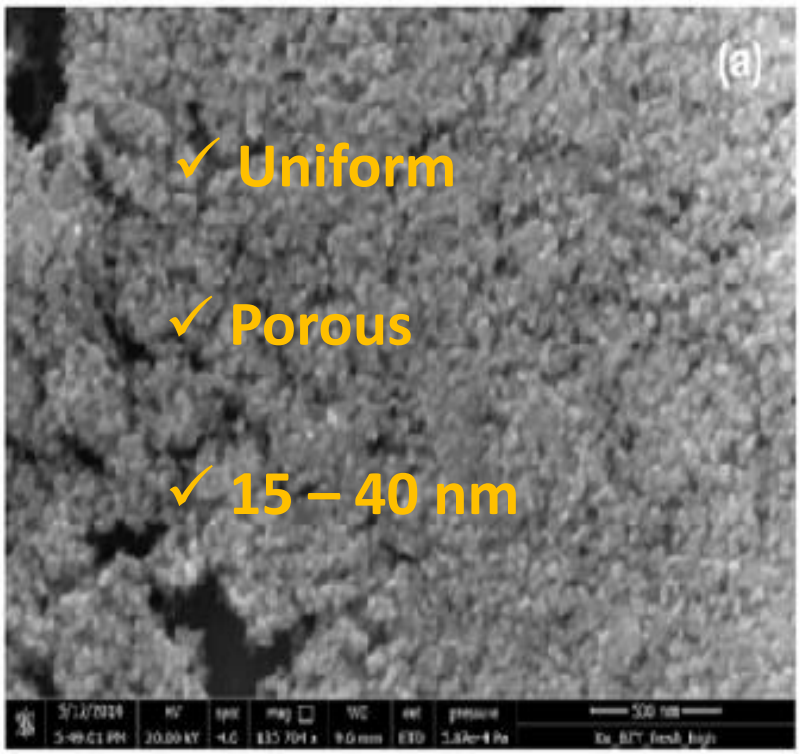
Counter electrode Au

- **Deposition with Au paste (Metalor A1118)**
- **Calcination at 650°C for 1 h**

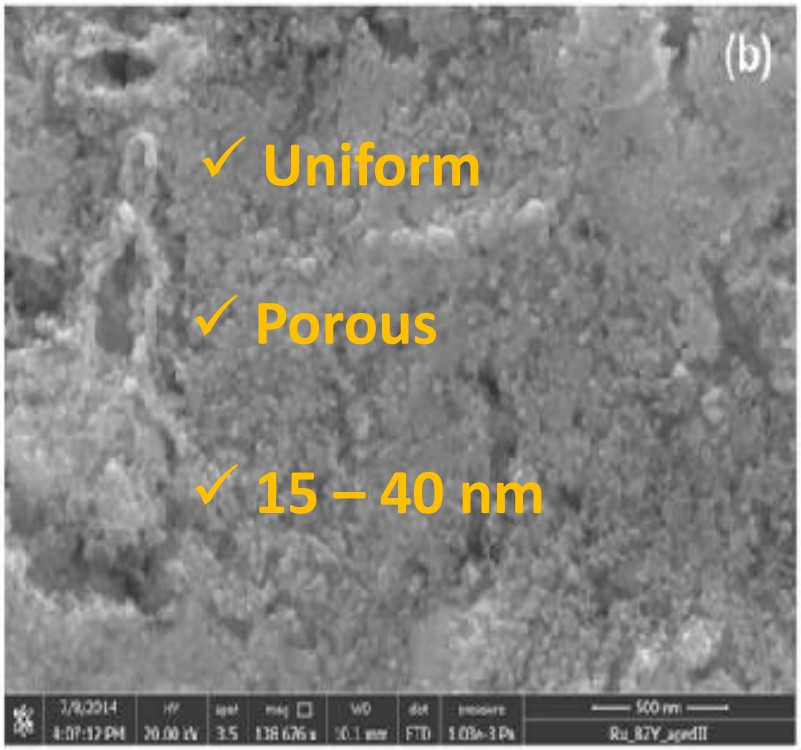
"Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions"
C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsiplakides, Kluwer Academic/Plenum Publishers, (2001).

Characterization of the catalyst
SEM – Ru/BZY(H^+)

fresh catalyst



used catalyst



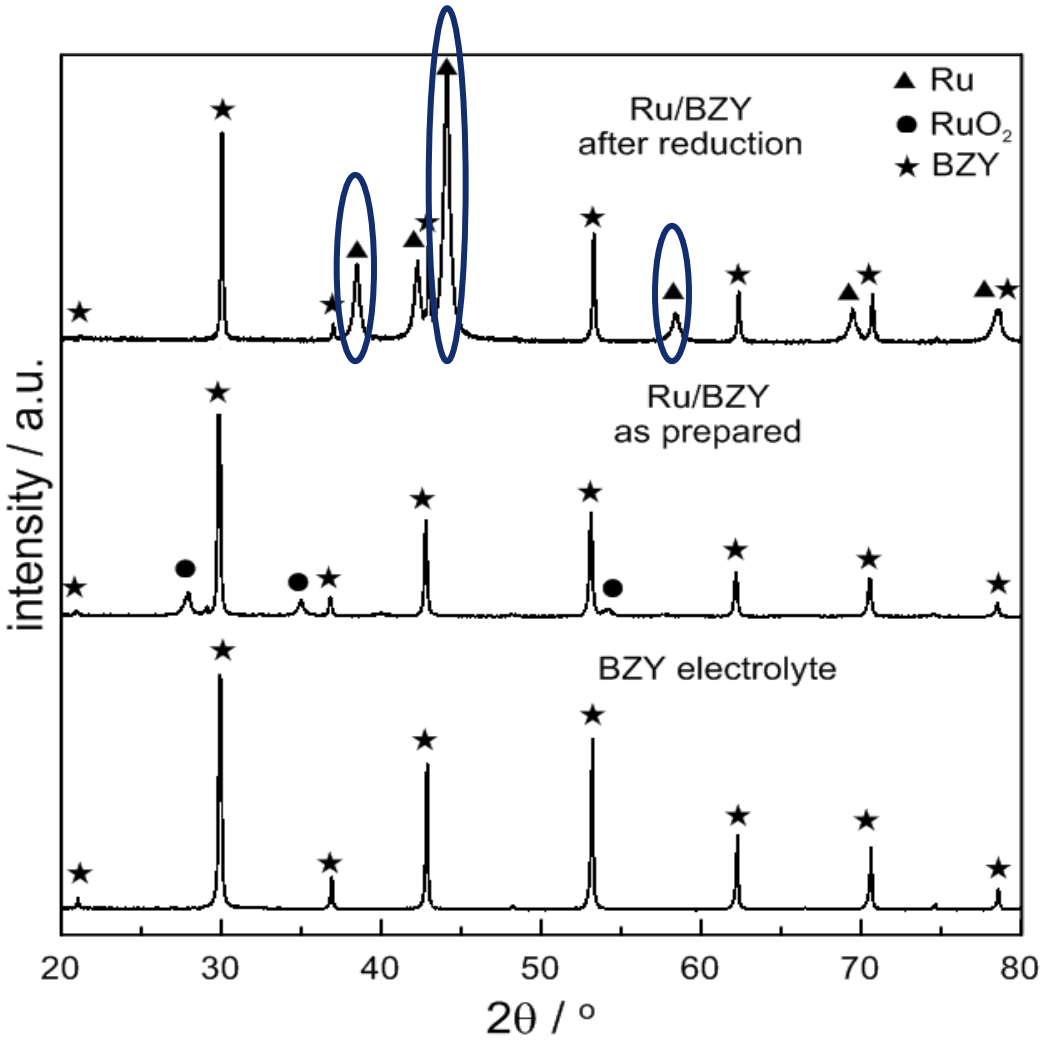
I. Kalaitzidou, A. Katsaounis, T. Norby, C.G. Vayenas, *J. Catal.* (2015) , submitted.

Characterization of the catalyst
XRD – Ru/BZY(H^+)

Scherrer equation

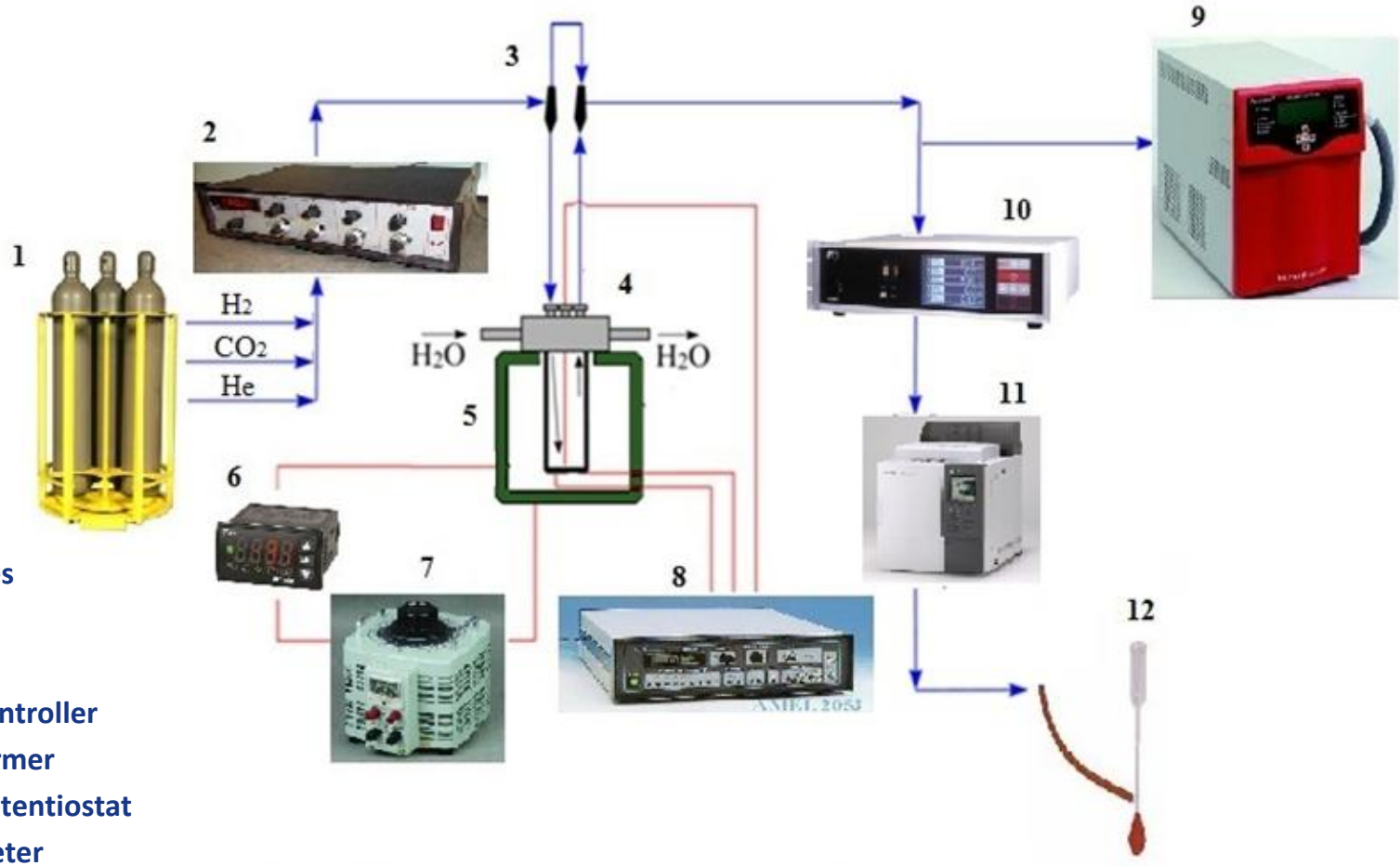
$$\tau = \frac{K \cdot \lambda}{\beta \cdot cos\theta}$$

20.6 ± 2 nm



I. Kalaitzidou, A. Katsaounis, T. Norby, C.G. Vayenas, *J. Catal.* (2015), submitted.

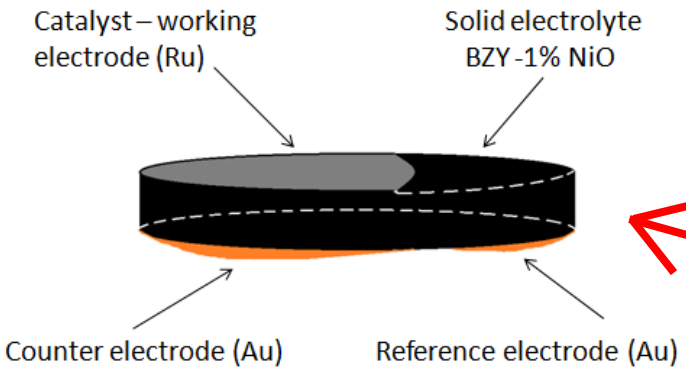
Experimental setup

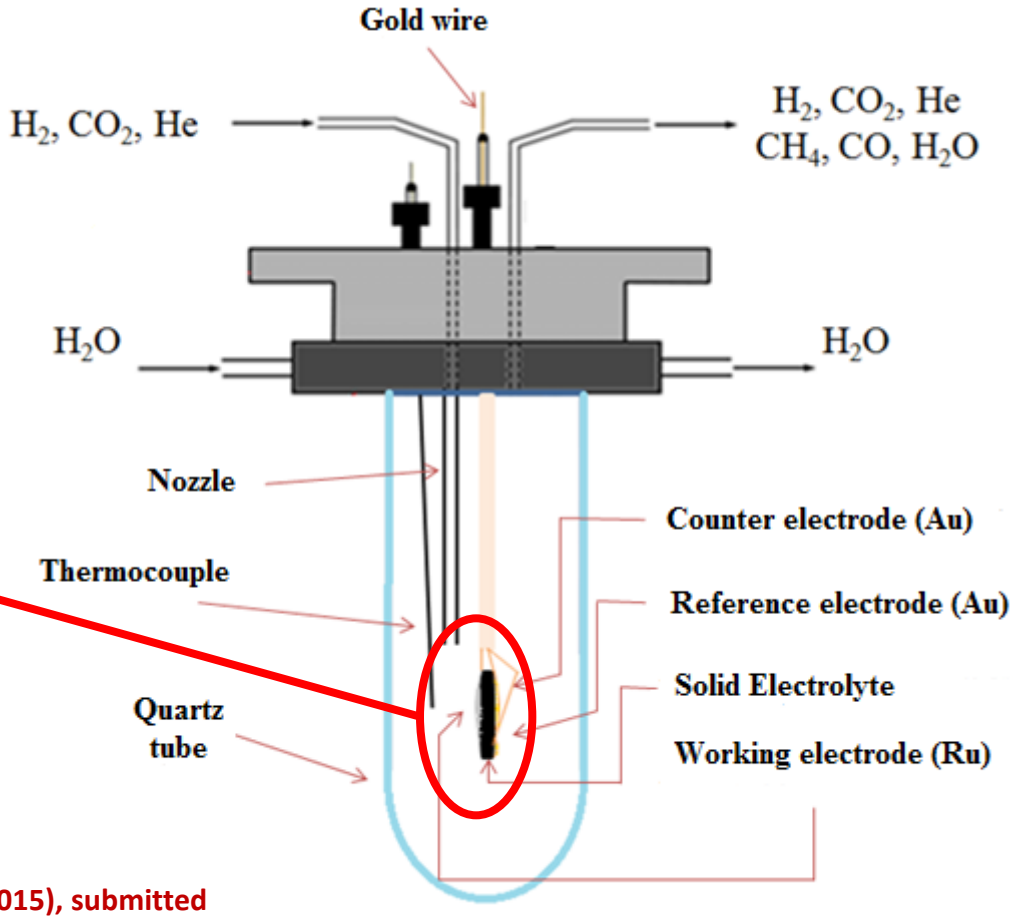


1. Gas bottles
2. Flow meters
3. Three way valves
4. Reactor
5. Furnace
6. Temperature controller
7. Voltage transformer
8. Galvanostat/ Potentiostat
9. Mass Spectrometer
10. IR analyzer
11. Gas chromatographer
12. Bubble meter

Electrochemical reactor
Single chamber

$BaZr_{0.85}Y_{0.15}O_3$ + 1 w% NiO





I. Kalaitzidou, A. Katsaounis, T. Norby, C.G. Vayenas, *J. Catal.* (2015), submitted

"Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions"
C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsiplakides, Kluwer Academic/Plenum Publishers, (2001).

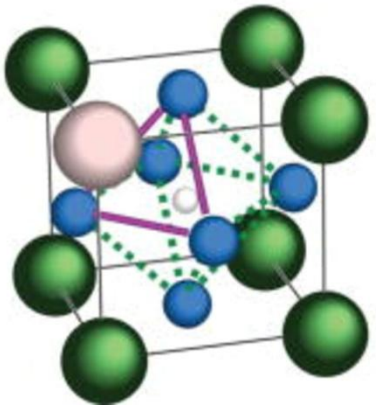
Preparation of electrochemical cells using BZY

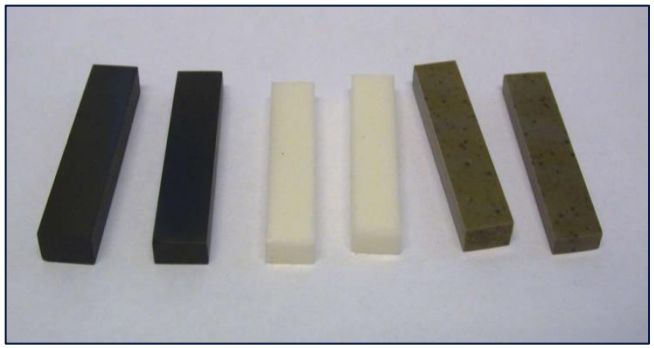
NorECs
Norwegian Electro Ceramics AS

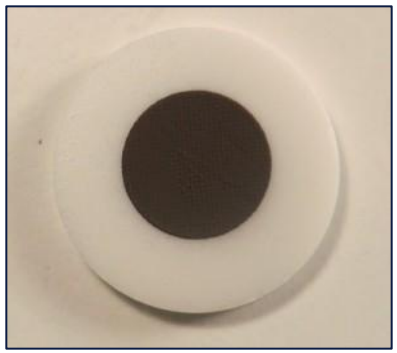
NorECs Norwegian Electro Ceramics AS

www.norecs.com

calcination of the nominal amounts of $BaCO_3$,
8YSZ (TOSOH) and 1 wt % NiO
at 1500°C for 12 hr
$BaZr_{0.8}5Y_{0.15}O_3$

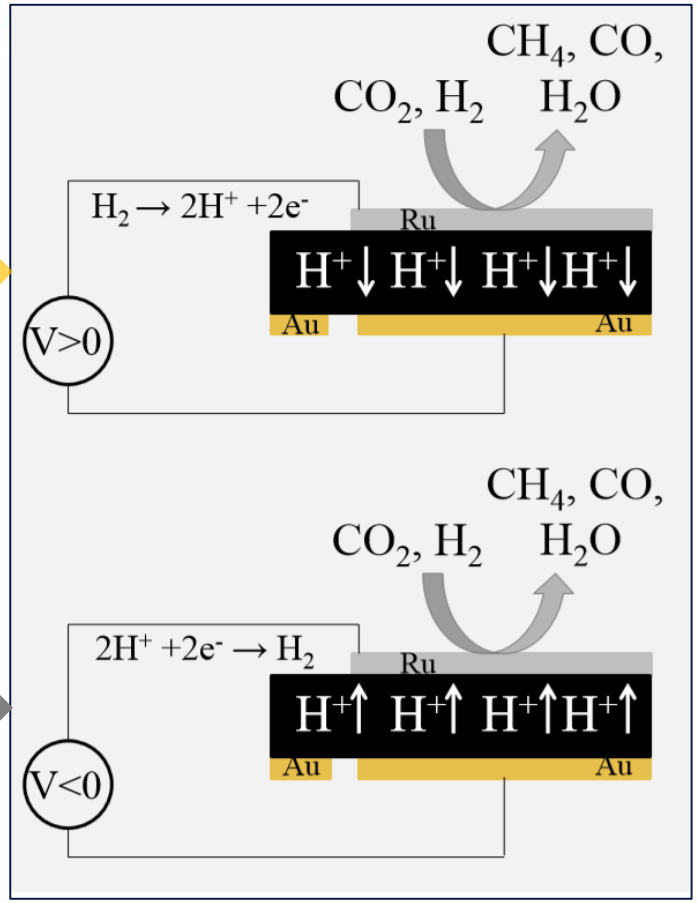


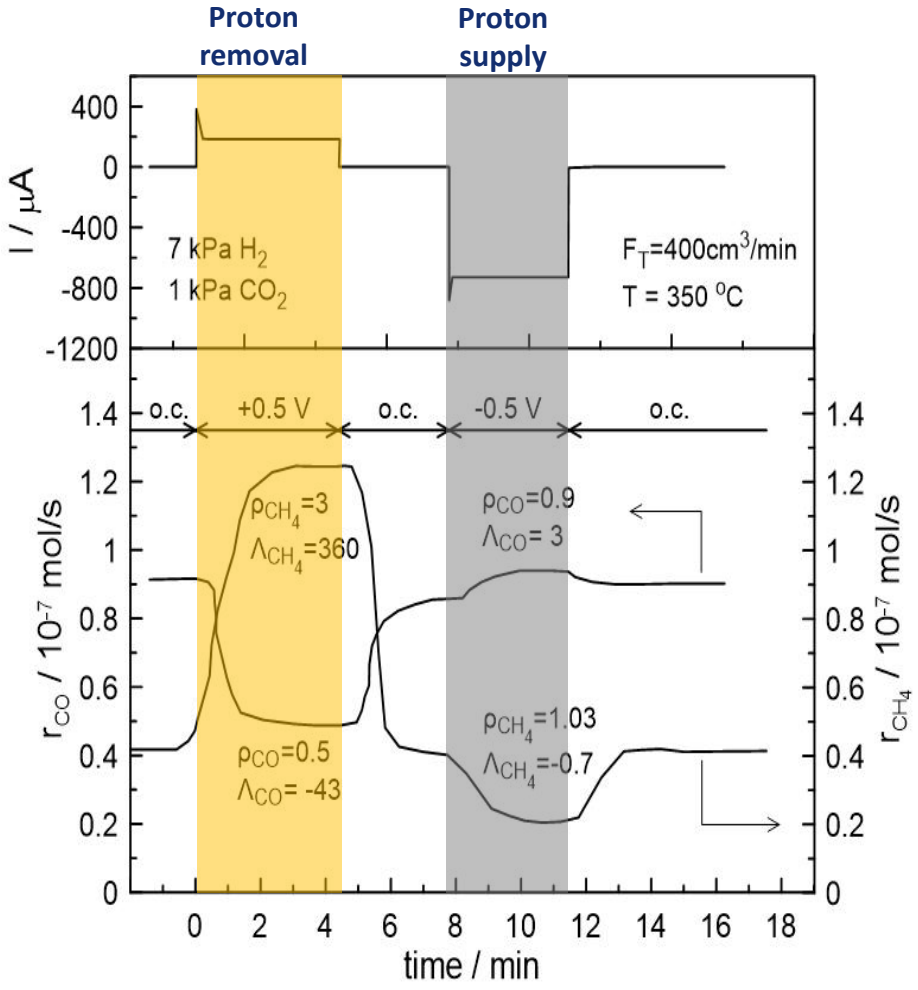




T.S. Bjørheim, A. Kuwabara, T. Norby, *J. Phys. Chem. C* 117 (2013) 5919-5930.
S. Erdal, C. Kongshaug, T.S. Bjørheim, N. Jalarvo, R. Haugsrud, T. Norby, *J. Phys. Chem. C*, 114 (2010) 9139-9145.
T. Norby, *Solid State Ionics* 125 (1999) 1-11.

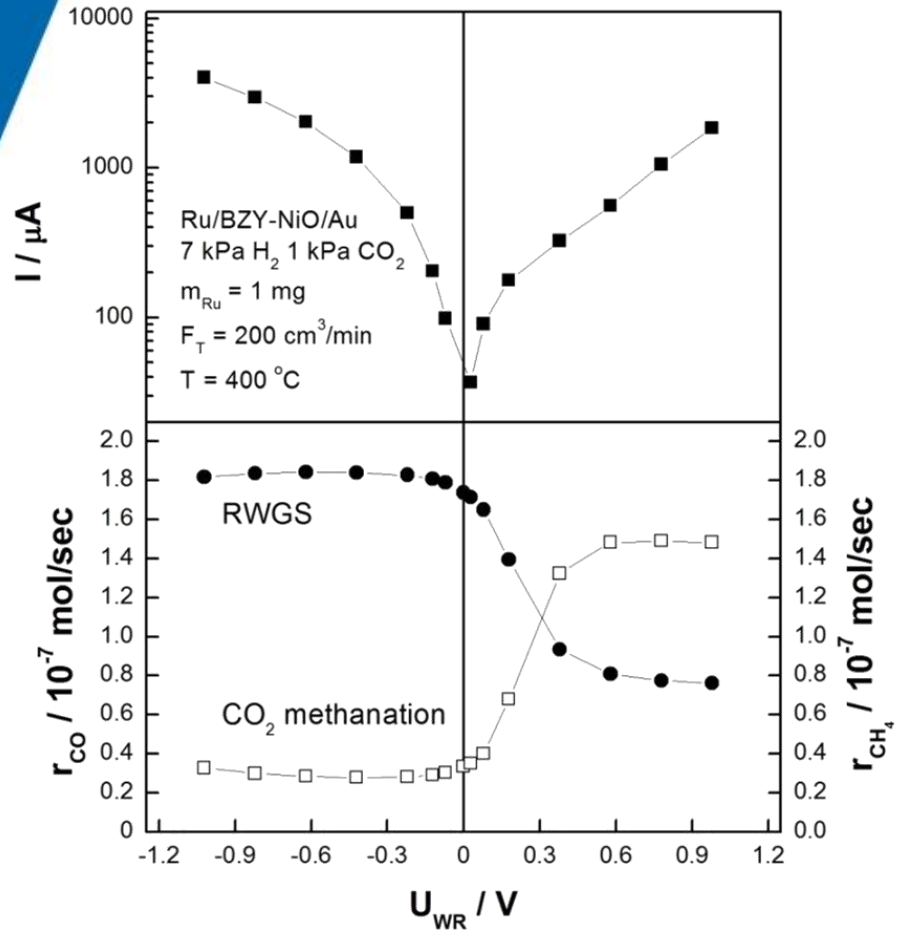
Effect of potential on r_{CH4} and r_{CO} Ru/BZY(H^+)

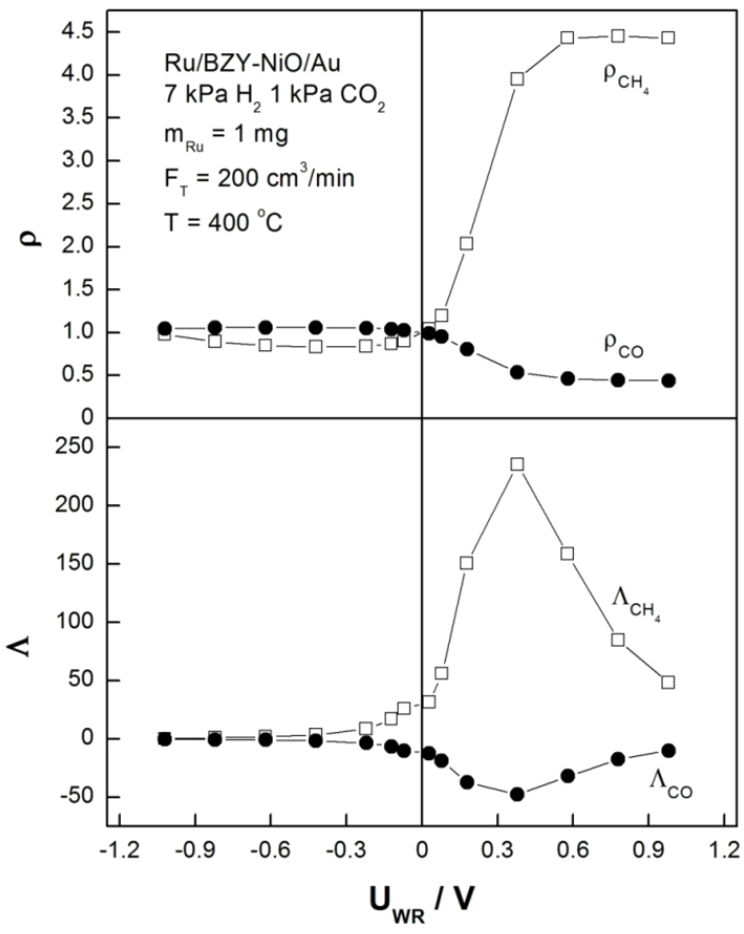




I. Kalaitzidou, A. Katsaounis, T. Norby, C.G. Vayenas, *J. Catal.* (2015), submitted.

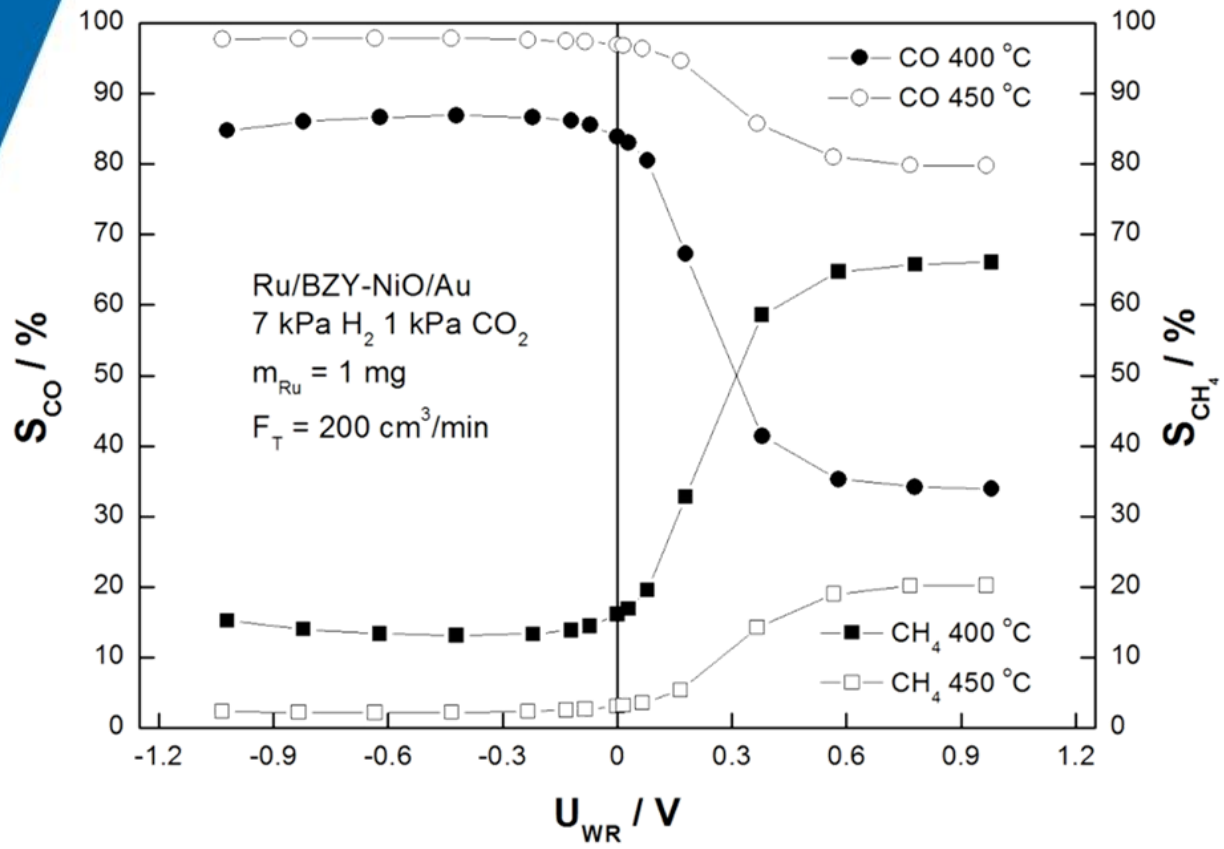
Effect of potential on r_{CH4}, r_{CO}, Λ, ρ Ru/BZY(H^+)





I. Kalaitzidou, A. Katsaounis, T. Norby, C.G. Vayenas, *J. Catal.* (2015), submitted.

Effect of potential on selectivity Ru/BZY(H^+)

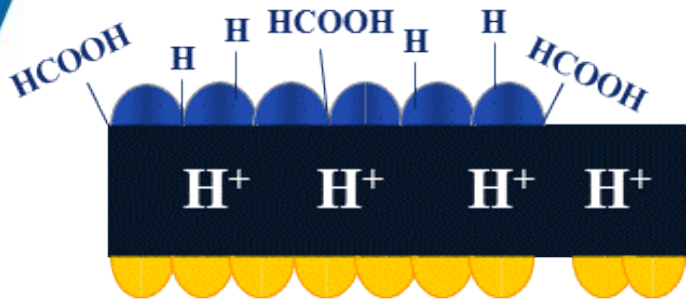


S_{CO} from 85 to 35%

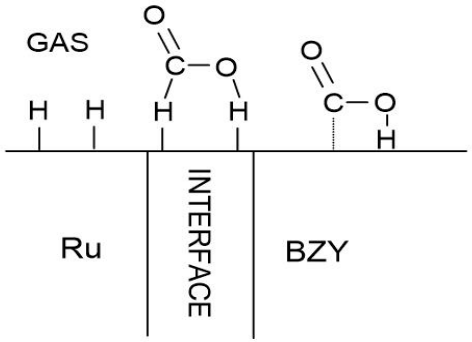
S_{CH_4} from 15 to 65%

I. Kalaitzidou, A. Katsaounis, T. Norby, C.G. Vayenas, *J. Catal.* (2015), submitted.

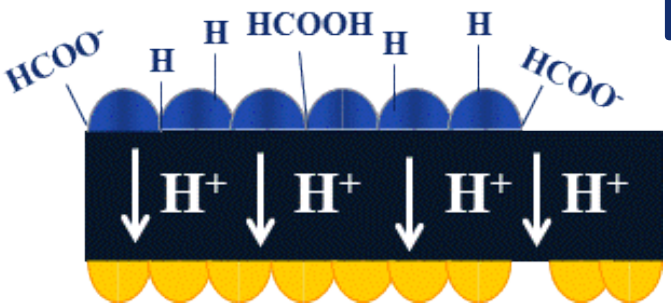
Mechanistic model Ru/BZY(H^+)



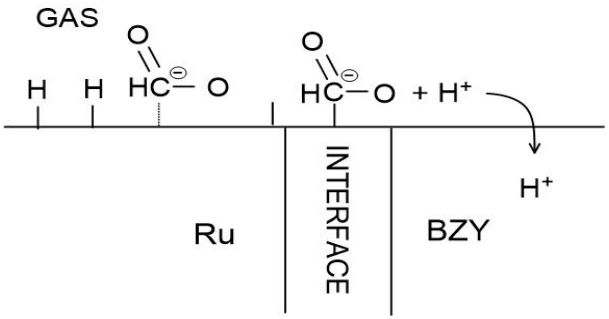
open circuit



+ e^- - H^+



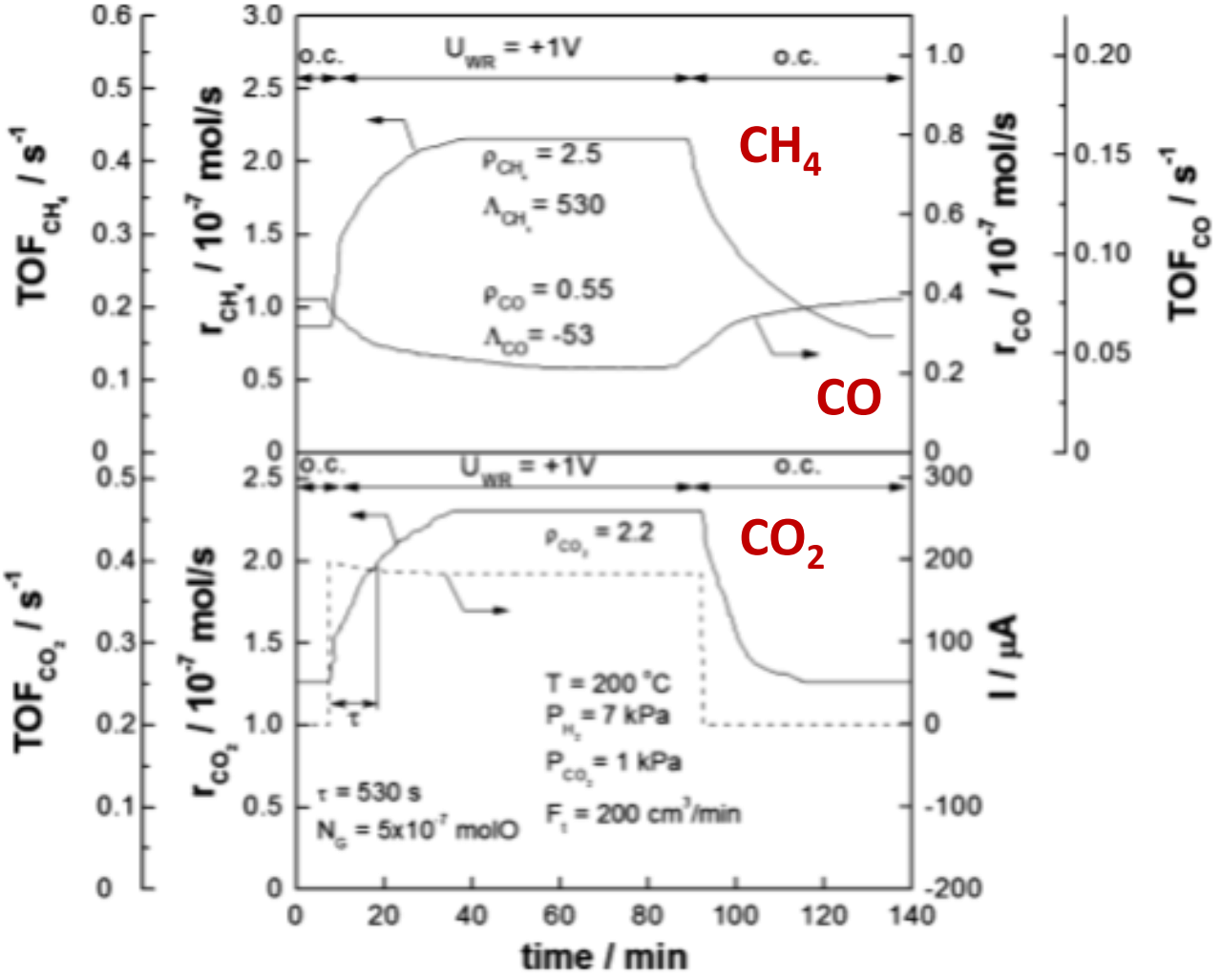
U > 0



I. Kalaitzidou, A. Katsaounis, T. Norby, C.G. Vayenas, *J. Catal.* (2015) submitted.
P. Panagiotopoulou, D.I. Kontarides, X.E. Verykios, *Catalysis Today* 181 (2012) 138-147.

Effect of potential on r_{CH4} and r_{CO} Ru/YSZ(O^{2-})

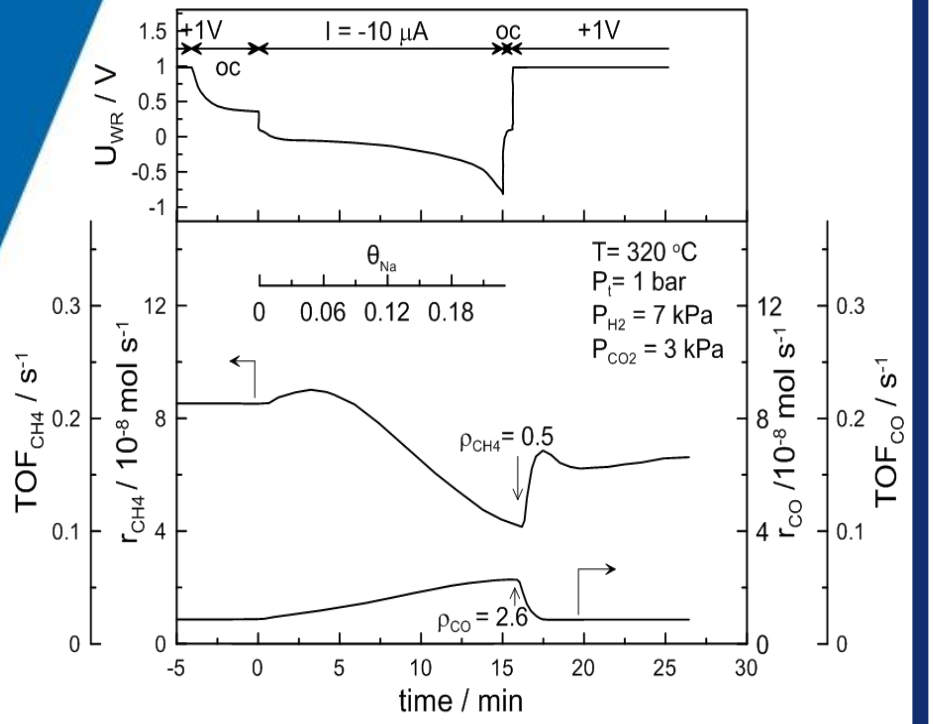
Positive potential application



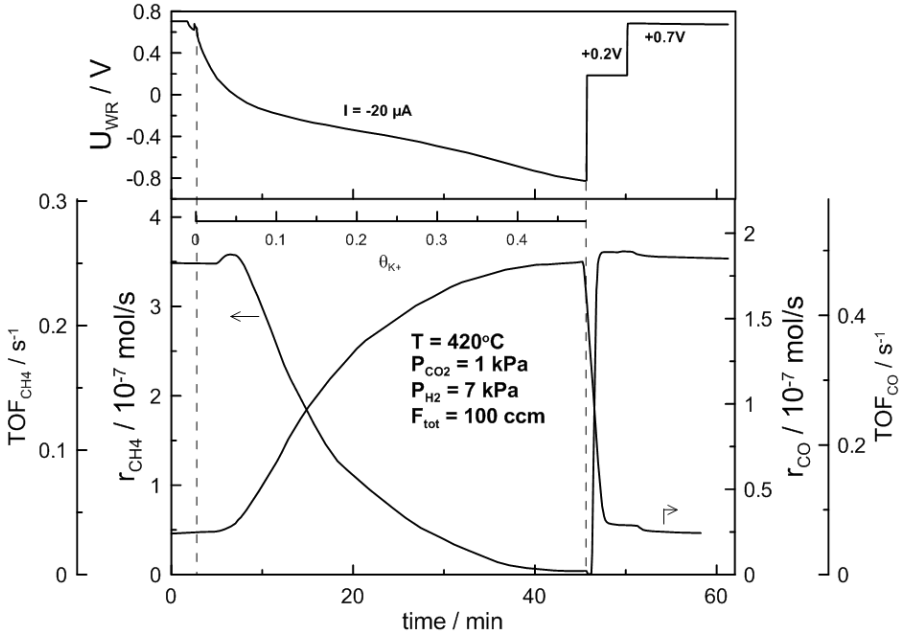
D. Theleritis, S. Souentie, A. Siokou, A. Katsaounis, C.G. Vayenas, *ACS Catalysis* 2 (2012) 770.

Effect of potential on r_{CH4} and r_{CO} Ru/β''-Al_2O_3

β''-Al_2O_3 (Na^+)



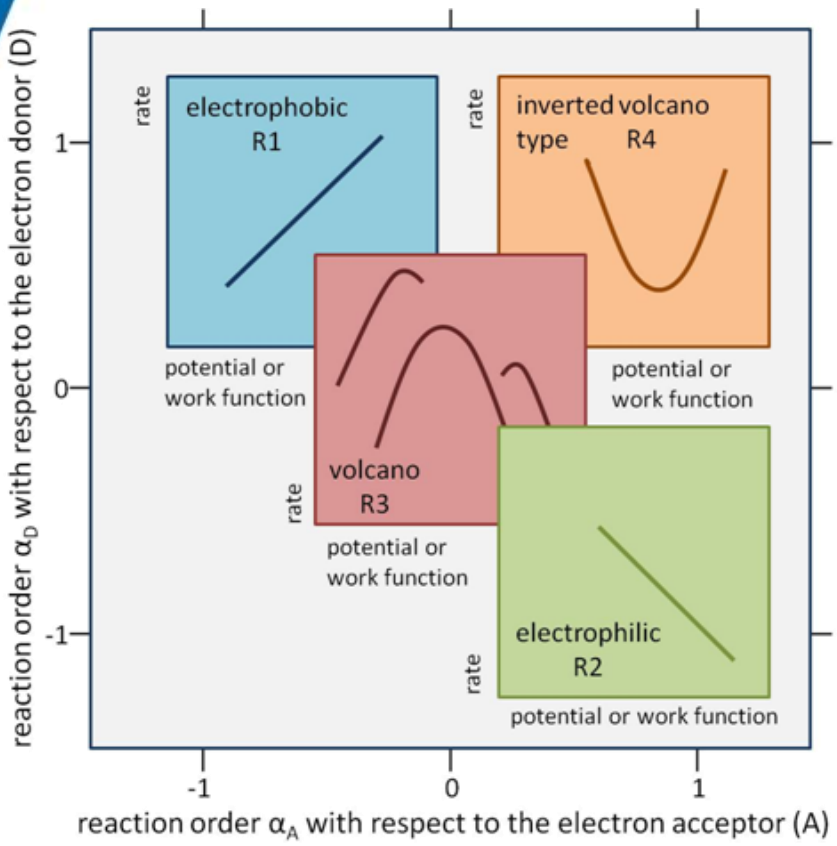
β''-Al_2O_3 (K^+)

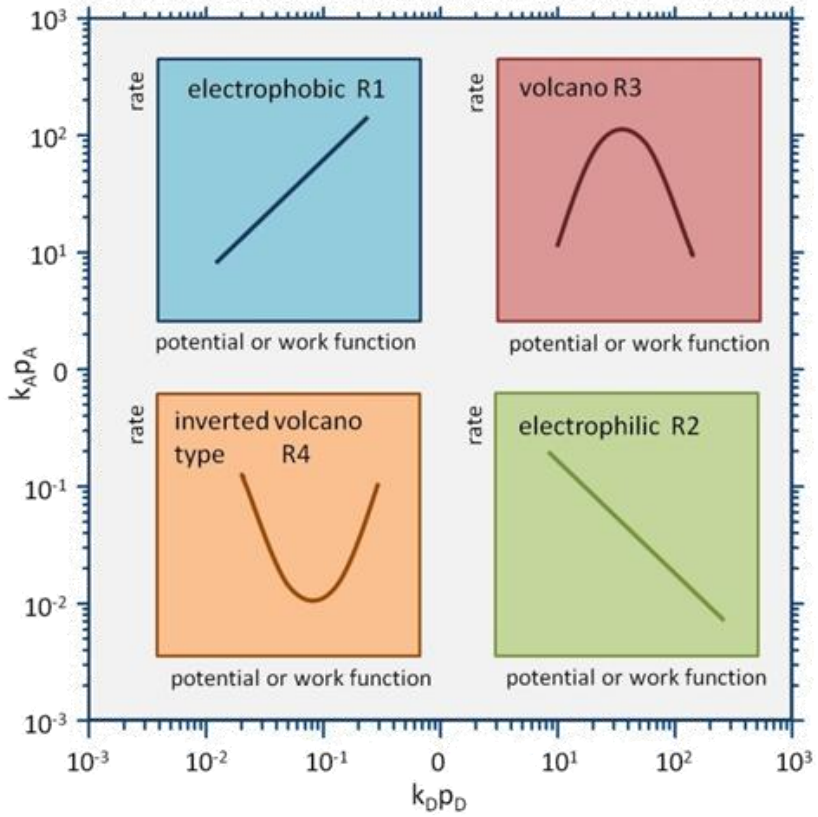


D. Theleritis, M. Makri, S. Souentie, A. Caravaca, A. Katsaounis, C.G. Vayenas, *ChemElectroChem* 1 (2014) 254.
M. Makri, A. Katsaounis, C.G. Vayenas (2015), in preparation.

Rules of Electrochemical & Chemical Promotion

RULES OF PROMOTION
IN TERMS OF REACTION ORDERS (LEFT)
OR IN TERMS OF ADSORPTION COEFFICIENTS (RIGHT)





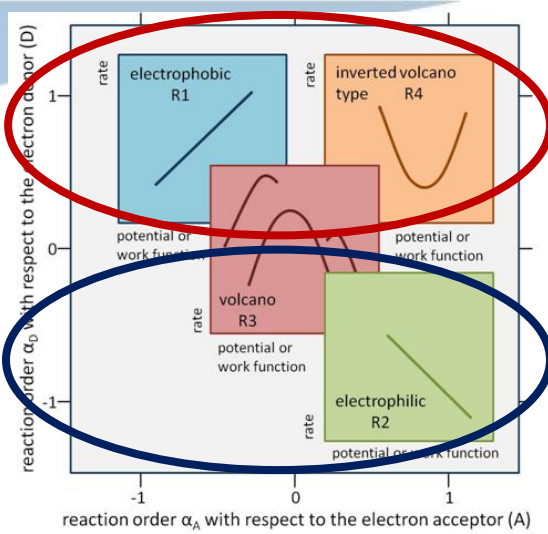
S. Brosda, C.G. Vayenas and J. Wei, *Appl. Catal. B* 68 (2006) 109.

Kinetic behaviour - predictions based on EPOC rules

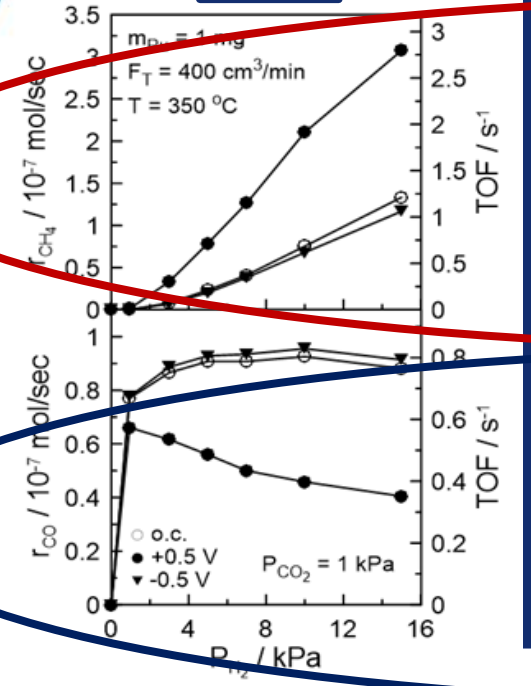
CH_4

CO

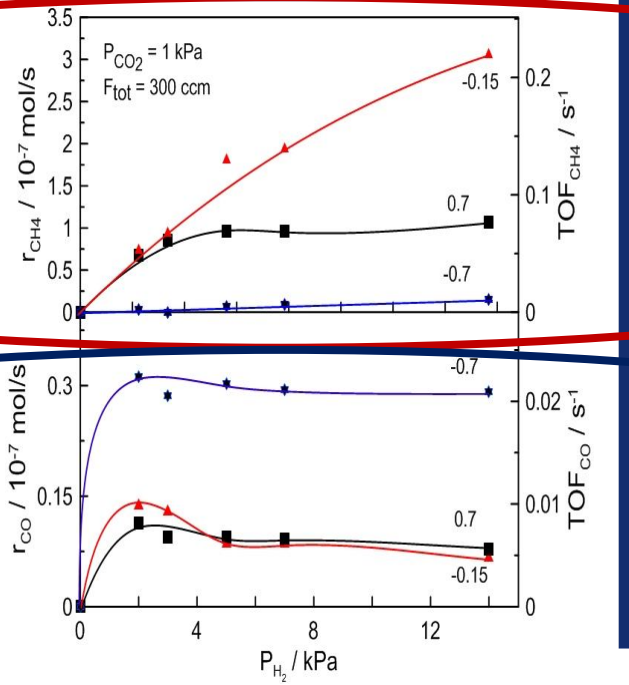
reaction (r_{CH4} and r_{CO}) order with respect to the electron donor, H_2



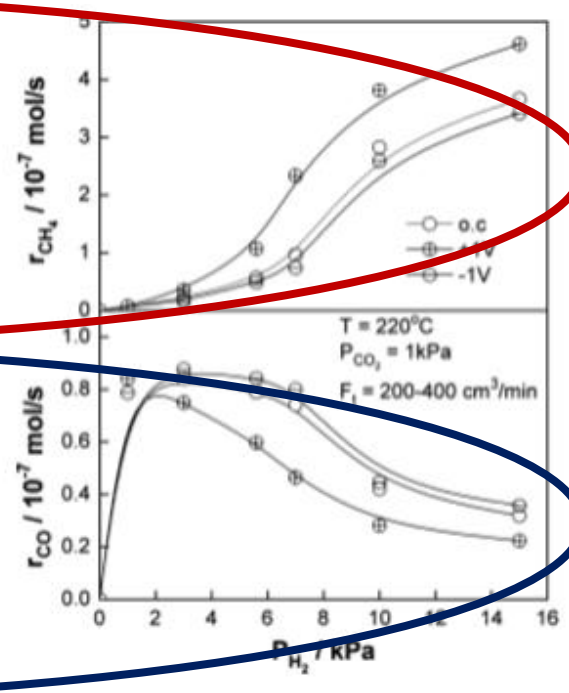
BZY



β'' - Al_2O_3



YSZ



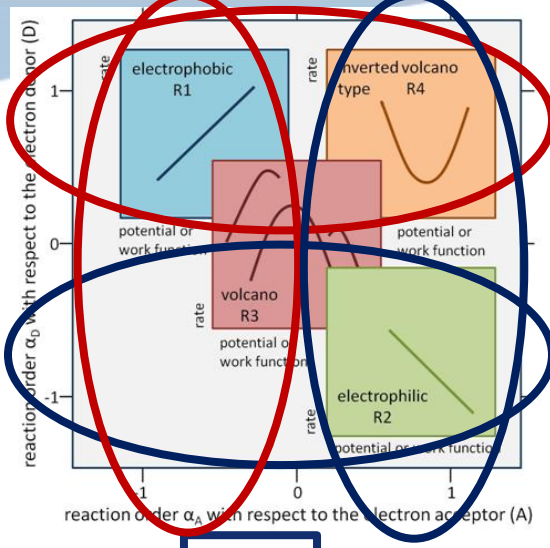
D. Theleritis, M. Makri, S. Souentie, A. Caravaca, A. Katsaounis, C.G. Vayenas, *ChemElectroChem* 1 (2014) 254.

M. Makri, A. Katsaounis, C.G. Vayenas, (2015), in preparation.

Kinetic behaviour - predictions based on EPOC rules

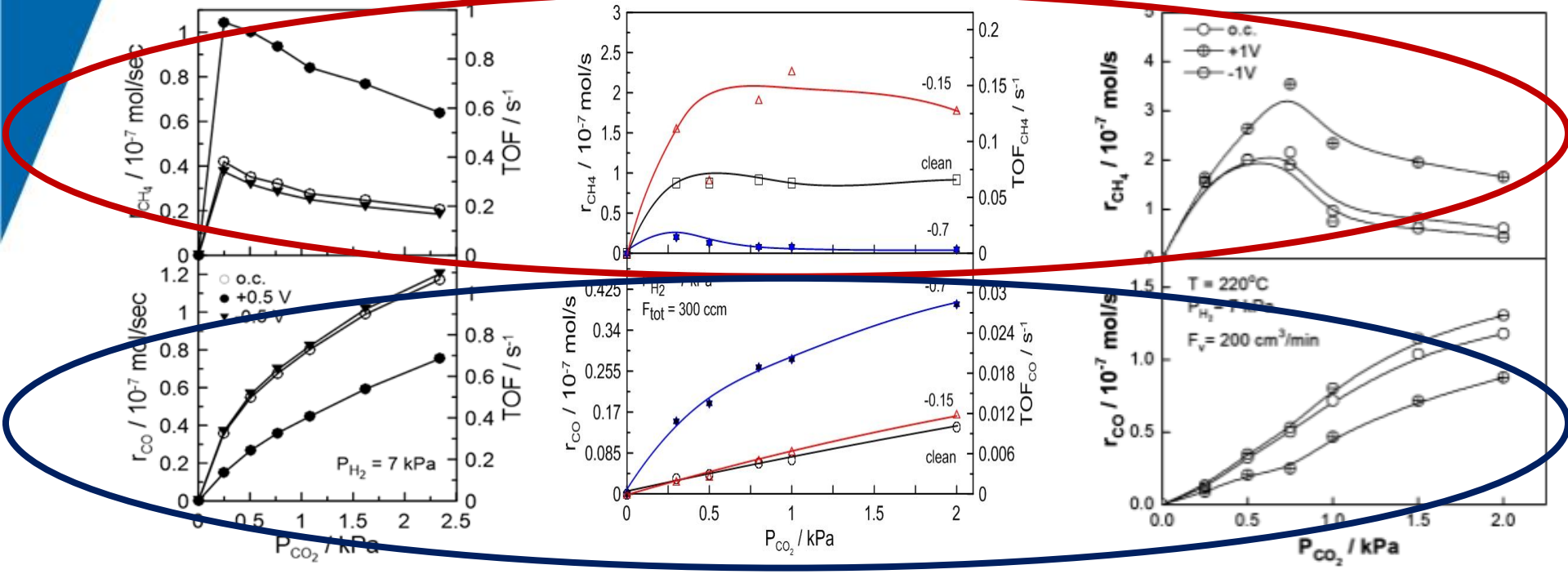
CH_4

CO



reaction (r_{CH4} and r_{CO}) order with respect to the electron acceptor, CO_2

BZY | **β'' - Al_2O_3** | **YSZ**



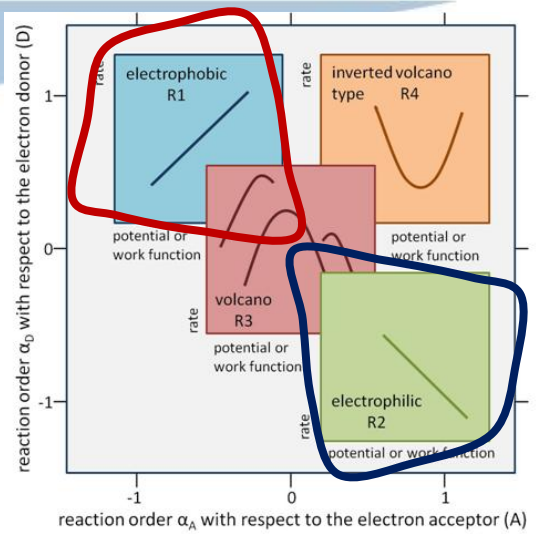
D. Theleritis, M. Makri, S. Souentie, A. Caravaca, A. Katsaounis, C.G. Vayenas, *ChemElectroChem* 1 (2014) 254.

M. Makri, A. Katsaounis, C.G. Vayenas, (2015) , in preparation.

Kinetic behaviour - predictions based on EPOC rules

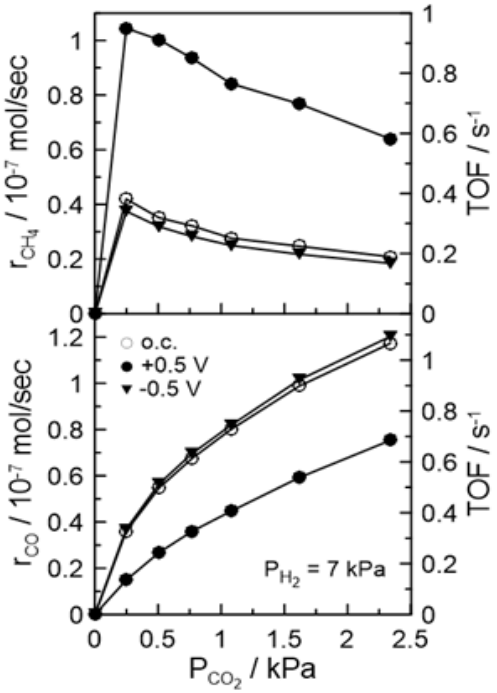
CH_4

CO

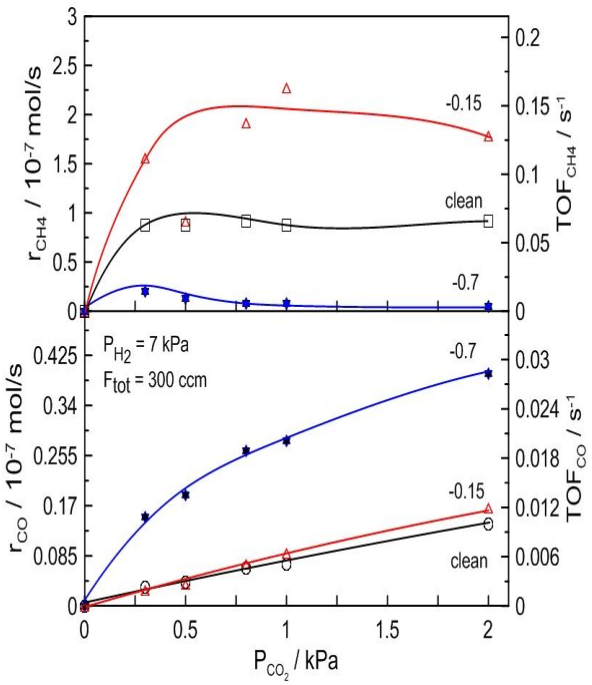


reaction (r_{CH4} and r_{CO}) order with respect to the electron acceptor, CO_2

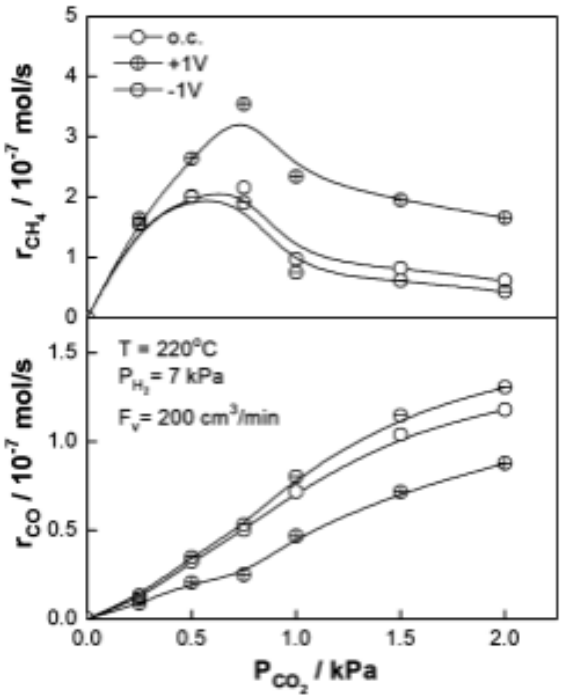
BZY



β'' - Al_2O_3



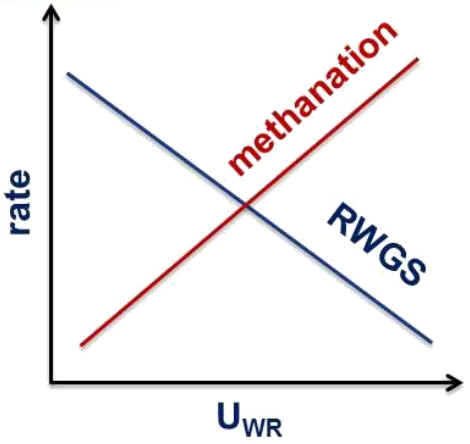
YSZ



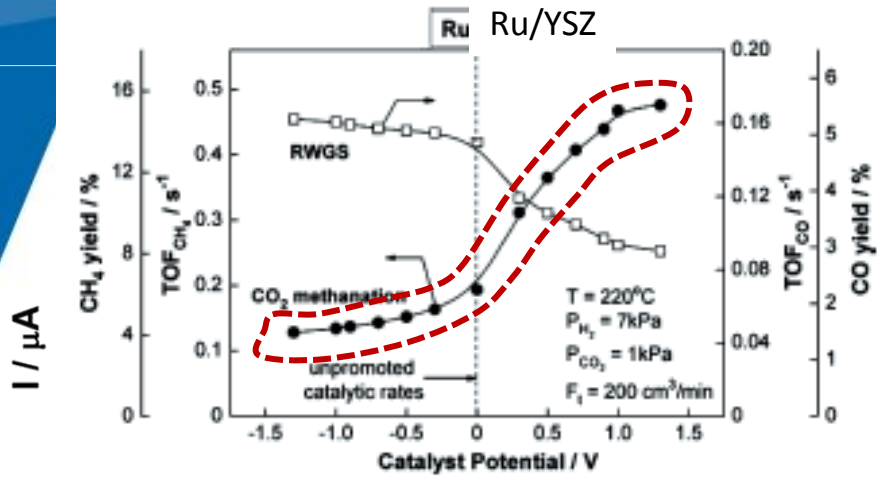
D. Theleritis, M. Makri, S. Souentie, A. Caravaca, A. Katsaounis, C.G. Vayenas, *ChemElectroChem 1* (2014) 254.

M. Makri, A. Katsaounis, C.G. Vayenas, (2015), in preparation.

Kinetic behaviour - predictions based on EPOC rules



Ru/YSZ



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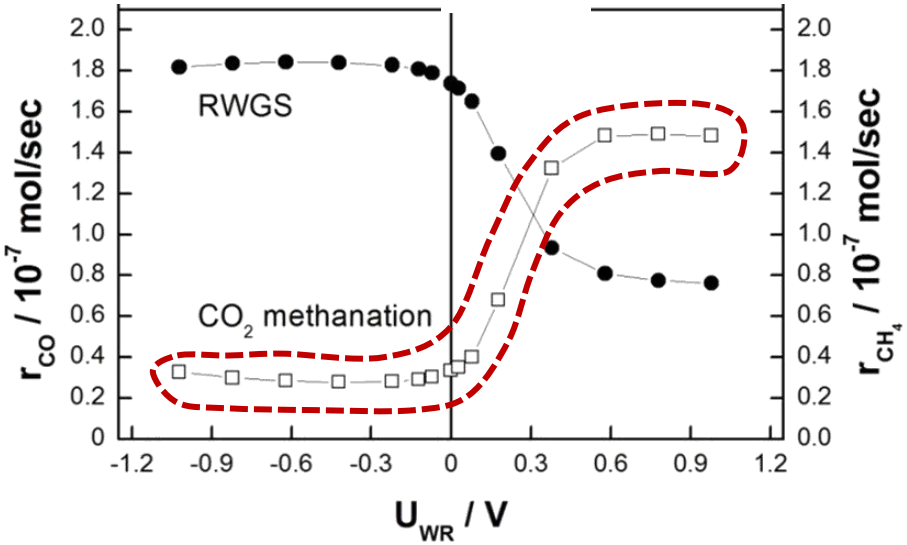

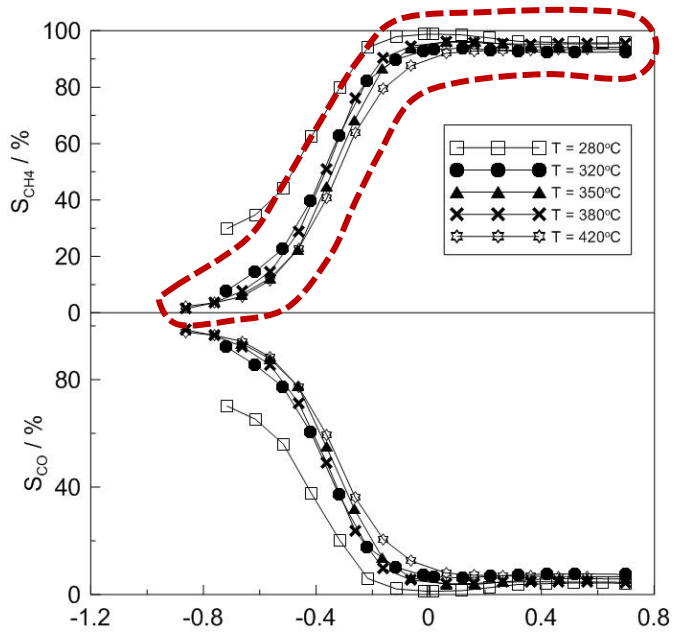

D. Theleritis, M. Makri, S. Souentie, A. Caravaca, A. Katsaounis, C.G. Vayenas, *ChemElectroChem* 1 (2014) 254.
M. Makri, A. Katsaounis, C.G. Vayenas, (2015), in preparation.

Conclusions

- ✓ Electrochemical promotion of CO_2 hydrogenation was explored on Ru supported catalysts using electronegative and electropositive promoters.
- ✓ Methane and carbon monoxide were the only measurable products under the investigated conditions.
- ✓ In all cases methane production followed electrophobic behaviour while CO formation followed electrophilic one.
- ✓ Rate enhancement ratios, ρ, up to 5 and Faradaic efficiency values, Λ, up to 250 were observed.

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Laboratory of Chemical & Electrochemical Processes

Department of Chemical Engineering

University of Patras, Greece

http://nemca.chemeng.upatras.gr

Alexandros Katsaounis

Dimitris Theleritis

Marialena Makri

Ioanna Kalaitzidou

Dimitris Grigoriou

Eftychia Martino

Alexandros Similides