Solid Electrolytes: Applications in Heterogeneous Catalysis and Chemical Cogeneration

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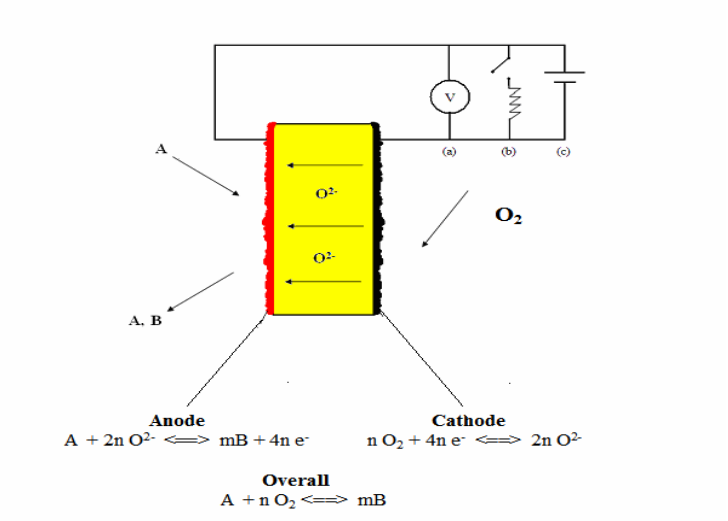
SOLID ELECTROLYTES

Solid materials that exhibit high ionic conductivity

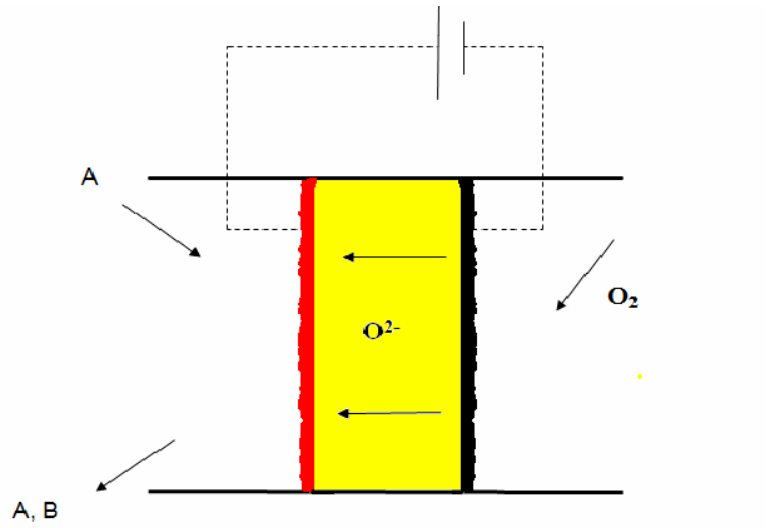
Cationic Conductors:	H^+, K^+, Na^+, Cu^+, Ag^+, Li^+
Anionic Conductors:	O^{2-}, F^-
Most Widely Used:	O^{2-} and H^+ conductors

"Pure" ionic:	$t_i/t_e > 100$
Mixed conductors:	O^{2-}-e^-, H^+- e^- , etc.

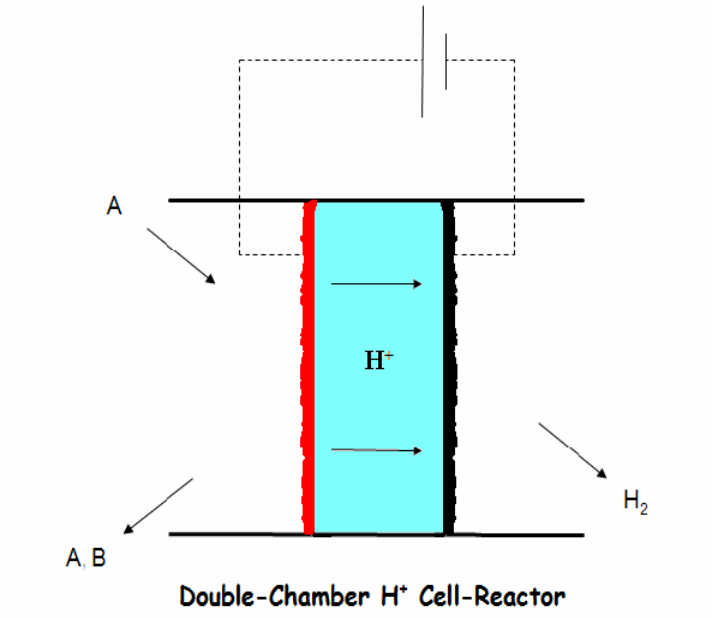
All these materials should be non porous (dense membranes). Ions are conducted through the lattice and not through the pores



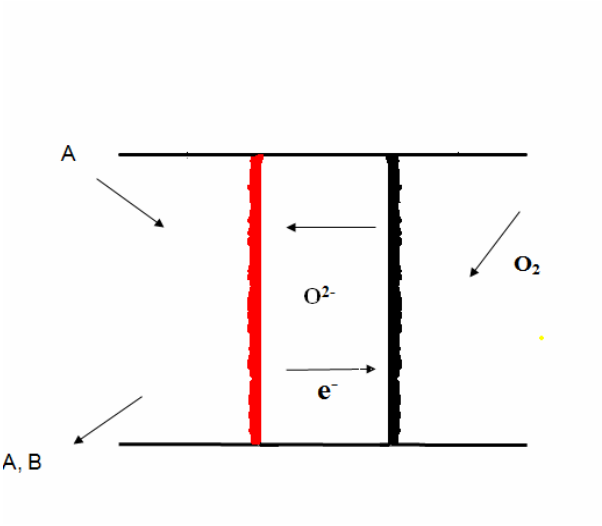
Applications: a)Sensors, b)Solid State Batteries,
c) Solid Oxide Fuel Cells, d) O_2 (H_2) Separators
e) **Solid Electrolyte Cell-Reactors**



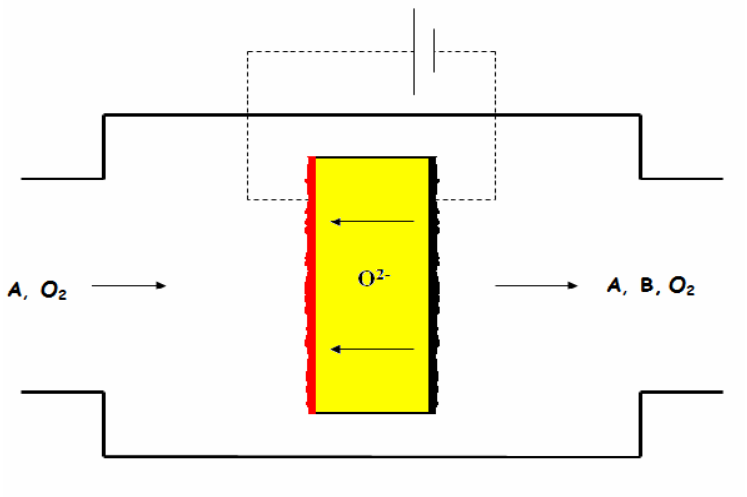
Double-Chamber Cell-Reactor
The two electrodes are exposed to different gaseous mixtures



Double-Chamber H^+ Cell-Reactor



Mixed (O^{2-} - e^-) Conducting Reactor
(No wires, net trasport of O atoms, not ions)



Single Chamber Cell (O^{2-}) Reactor
Both electrodes exposed to the same gaseous mixture

Catalytic Studies in SECRs

1) CH_4 to C_2's; CH_4 to CO and H_2; CH_4 combustion
2) Partial and deep oxidation of alkanes
3) Partial and deep oxidation of alkenes
4) Decomposition of NO_X; NO_X reduction by HCs
5) CO oxidation; CO_2 dissociation
6) H_2 oxidation; Steam electrolysis
7) Forward and Reverse Water Gas Schift
8) NH_3 synthesis; NH_3 oxidation; HCN synthesis
9) H_2S Decomposition; H_2S Oxidation; SO_2 Oxidation
10) Oxidation and hydrogenation of aromatic compounds
11) Oxidation and decomposition of alcohols

The goals of these studies

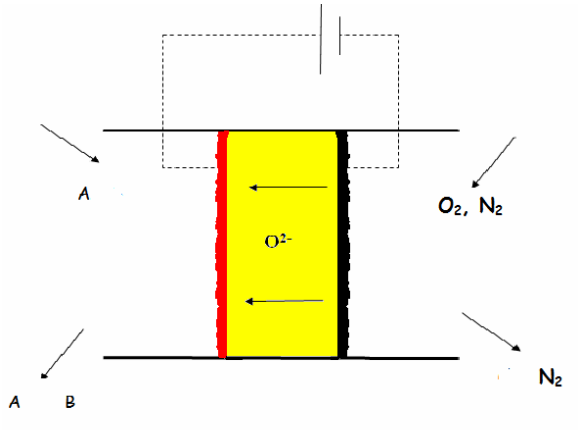
1) Take advantage of the selective conduction of ions.

2) Investigate the mechanism of the catalytic reaction.

3) Improve the yield to the desired product by operating under closed circuit.

4) Accummulate knowlegde in order to scale up these processes.

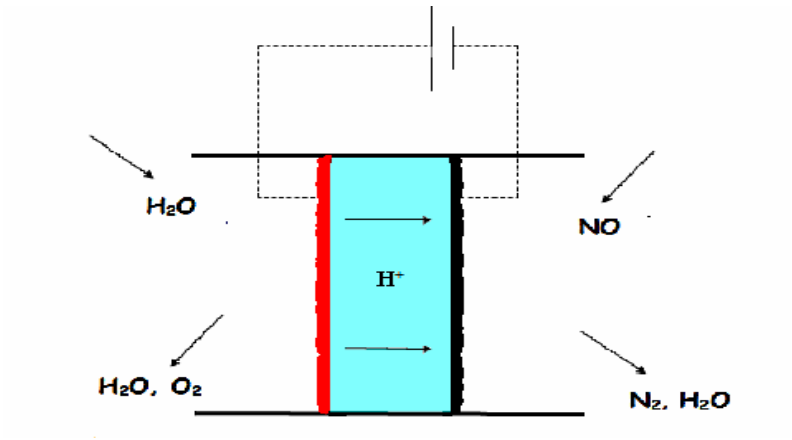
Selective conduction of O^{2-}: separate O_2 and N_2 (air)



Cathode: n O_2 + 4n e^- <==> 2n O^{2-} Anode: 2n O^{2-} + A <==> m B + 4n e^-

Overall: A + n O_2 <==> m B

Selective conduction of H^+: NO reduction by steam

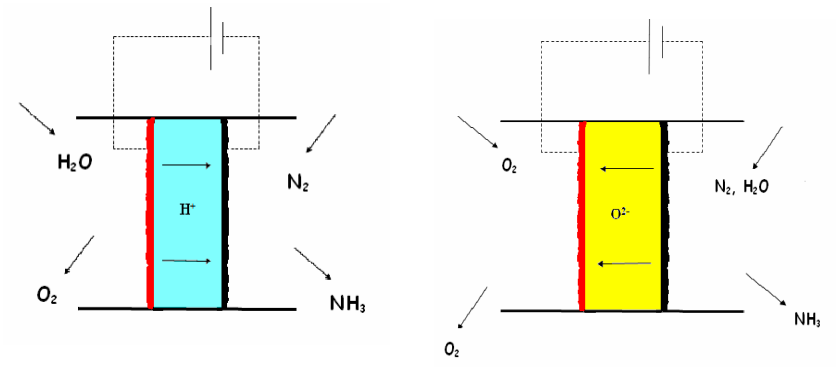


Anode: $2H_2O$ <==> $O_2 + 4H^+ + 4e^-$ Cathode: $2NO + 4H^+ + 4e^-$ <==> $N_2 + 2H_2O$

Overall: $2\ NO$ <==> $N_2 + O_2$

From: T. Kobayashi, et al, Solid State Ionics 134 (2000) 241-247

Ammonia synthesis from steam and nitrogen



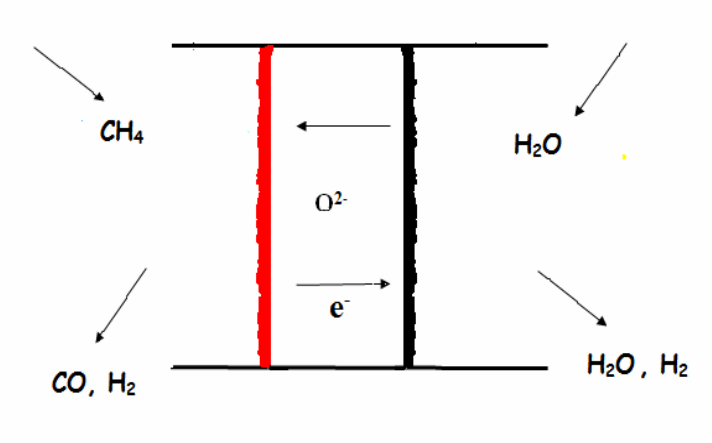
Anode: $6H_2O$ <==> $3O_2 + 12H^+ + 12e^-$
Cathode: $2\ N_2 + 12\ H^+ + 12\ e^-$ <==> $4\ NH_3$

Cathode: $2N_2 + 6H_2O + 12e^-$ <==> $4NH_3 + 6O^{2-}$
Anode: $6O^{2-}$ <==> $3O_2 + 12e^-$

Overall: $2\ N_2 + 6\ H_2O$ <==> $4\ NH_3 + 3\ O_2$

From: A. Skodra, et al, Solid State Ionics, *Solid State Ionics* ***180*** *(2009)1332-1336*)

H_2O splitting and CH_4 conversion to CO and H_2

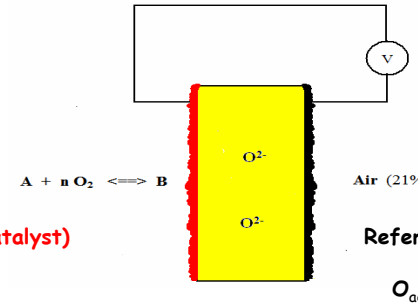


Right: $H_2O + 2\ e^- \text{ <==> } O^{2-} + H_2$ Left: $CH_4 + O^{2-} \text{ <==> } CO + 2\ H_2 + 2\ e^-$

Overall: $CH_4 + H_2O \text{ <==> } CO + 3\ H_2$

From: H. Jiang, et al, Angew. Chem. Int. Ed. 47 (2008) 9341-9344

Open circuit (I = 0) studies of the reaction mechanism



Working electrode (catalyst)

$O_2 \Leftrightarrow 2\ O_{ads}$

$O_{ads} + 2\ e^- \Leftrightarrow O^{2-}$

$A + O_{ads} \Leftrightarrow B$

$P_{O2(c)} > a_{o(c)}^2$

Reference electrode (air)

$O_2 \Leftrightarrow 2\ O_{ads}$

$O_{ads} + 2\ e^- \Leftrightarrow O^{2-}$

$P_{O2(r)} = a_{o(r)}^2$

$\mu_{O(c)} - \mu_{O(r)} = 2FE$

$RT\ln a_{o(c)} - RT\ln a_{o(r)} = 2FE$

$a_{o(c)} = (0.21)^{0.5} \exp(2FE/RT)$

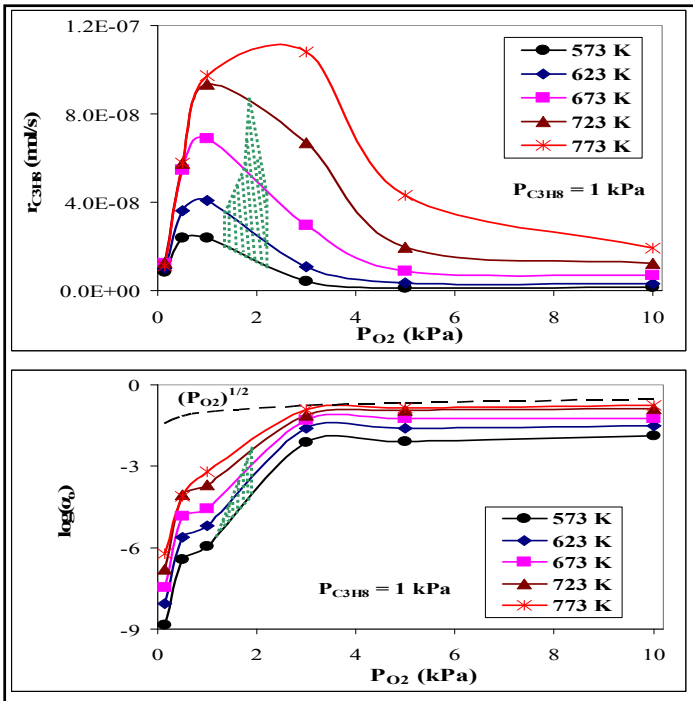
Solid Electrolyte Potentiometry (SEP)

1) in situ technique

2) continuous measurement of a_o

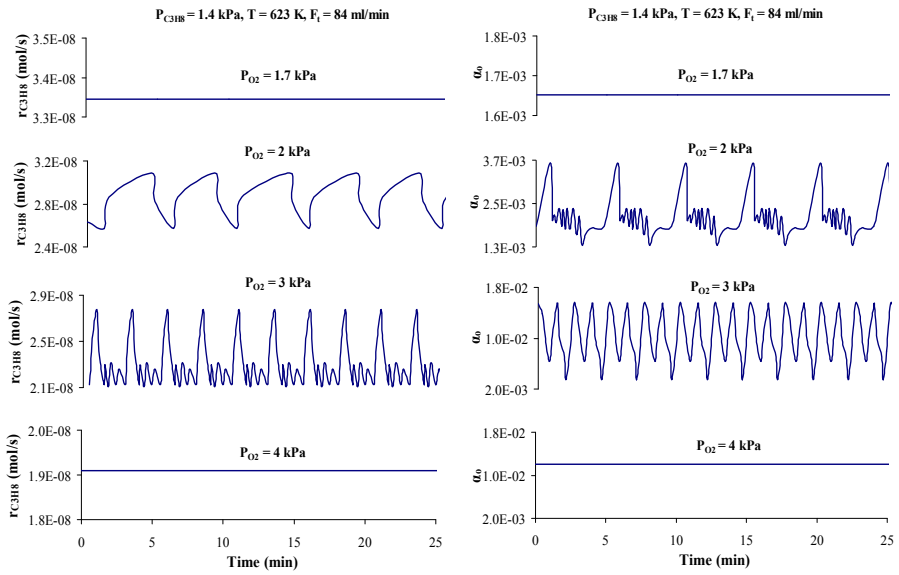
Solid Electrolyte Potentiometry Studies (1979-)

Catalytic Reaction	Catalyst (electrode)
$SO_2 + ½\ O_2 \rightarrow SO_3$	Pt, Au, Ag
$CO + ½\ O_2 \rightarrow CO_2$	Pt, Ag, $Cu\text{-}Cu_2O\text{-}CuO$
$H_2 + ½\ O_2 \rightarrow H_2O$	Ni, Ag, $Cu\text{-}Cu_2O\text{-}CuO$
$2\ NO \rightarrow N_2 + O_2$	Pt, Pd
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	Pt, Au, Ag, Pd
$C_2H_4O + 2.5\ O_2 \rightarrow 2CO_2 + 2H_2O$	Ag
$C_2H_4 + 3\ O_2 \rightarrow 2CO_2 + 2H_2O$	Ag, Pt
$C_2H_4O + 2.5\ O_2 \rightarrow 2CO_2 + 2H_2O$	Ag
$C_2H_4 + 3\ O_2 \rightarrow 2CO_2 + 2H_2O$	Ag, Pt
$C_3H_6 + 4.5\ O_2 \rightarrow 3CO_2 + 3H_2O$	Ag, Pt
$C_3H_6O + 4\ O_2 \rightarrow 3CO_2 + 3H_2O$	Ag
$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O$	$Cu\text{-}Cu_2O\text{-}CuO$, $Fe_2O_3\text{-}Sb_2O_4$
$C_3H_8 + 5\ O_2 \rightarrow 3CO_2 + 4H_2O$	Pd, Pt, Ag
$C_3H_4O + ½\ O_2 \rightarrow C_3H_3OOH$	$Mo_{12}V_3Cu_{22}O_{44}$
$C_3H_8 + ½\ O_2 \rightarrow C_3H_6 + H_2O$	$Mg_2V_2O_7$



Propane oxidation on Pt

From:
C. Kokkofitis et al,
J. Catalysis, *234, (2005) 476*;
J. Catalysis, *243, (2006) 428*;



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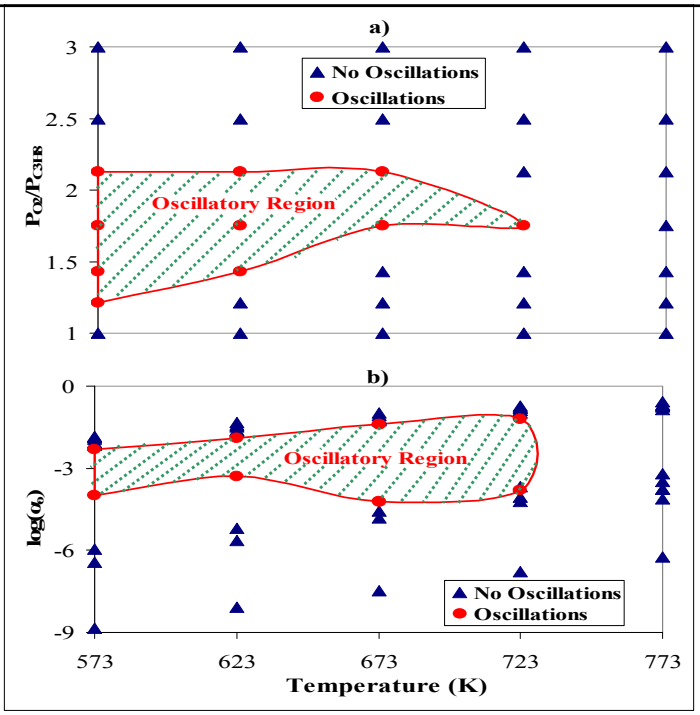

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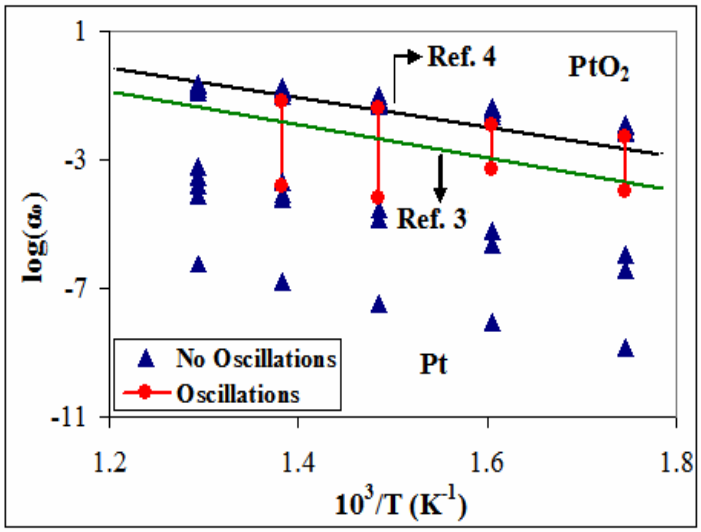

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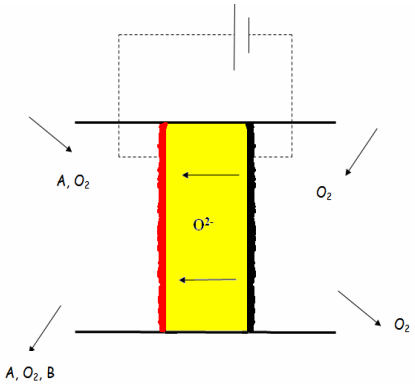
C. Kokkofitis et al, J. Catalysis, *234, (2005) 476* ; J. Catalysis, *243, (2006) 428* ;
Ref. 3 : C.G.Vayenas and J.N. Michaels, Surface Science, **120** (1982) L405.
Ref. 4: R.J. Berry, Surface Science, **76** (1978) 415.

Closed circuit operation. Faradaic & Non-Faradaic Effects.

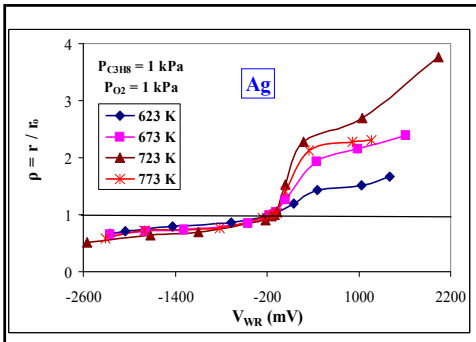


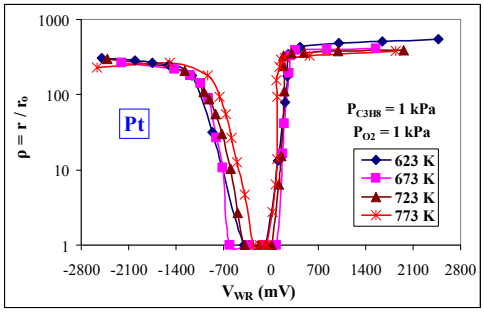
$$A + n\ O_2 \ <==>\ m\ B$$

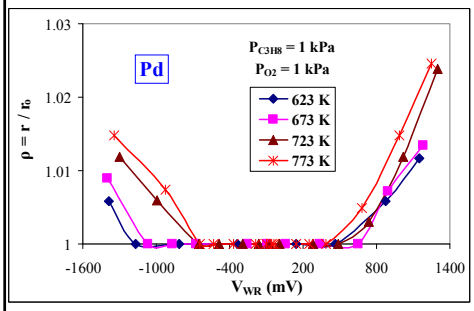
r_o: Open-circuit (I=0) rate (mol O_2/s)
r : Closed-circuit rate >> >>
I/4F = rate of O_2 transport >> >>
$\Delta r = r - r_o$ >> >>

$$\Lambda = \Delta r / (I/4F)$$
$$\rho = r/r_o$$

$\Lambda = 1$: $\Delta r = r - r_o = I/4F$ ➔ Faradaic Behavior
$\Lambda > 1$: $r - r_o > I/4F$ ➔ Non-Faradaic Behavior, Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA)







Propane oxidation on Ag, Pt and Pd

Ag : purely electrophobic
$1 < \Lambda < 10$ $1 < \rho < 10$

Pt : "inverted volcano"
$1 < \Lambda < 1000$ $1 < \rho < 1200$

Pd : "inverted volcano"
$0.5 < \Lambda < 1.2$ $1 < \rho < 1.1$

*From: Topics in Catalysis, **44** (2007) 361-368.*

Electrochemical Promotion of Catalysis (NEMCA)

Since 1981, more than 70 different catalytic reaction systems have been electrochemically promoted on

Pt, Rh, Pd, Ag, Au, Fe, Ni, RuO_2, IrO_2

catalysts deposited on

O^{2-}, H^+, Na^+, K^+, F^- and mixed (O^{2-}, e^-)

conductors using either

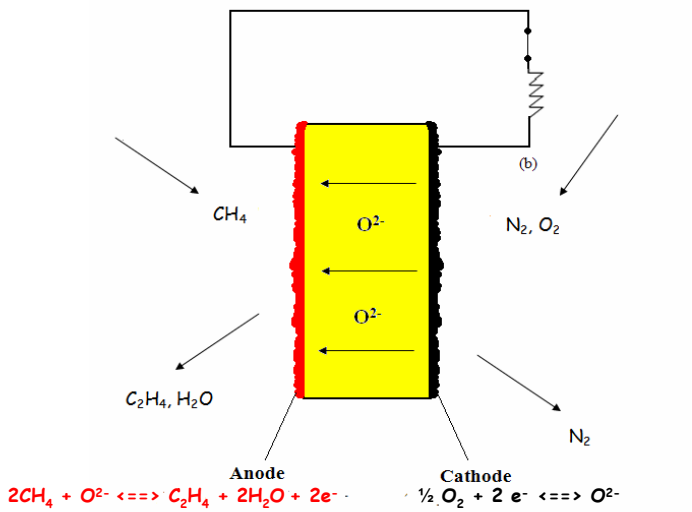
double or single-chamber cell-reactors.

Λ values as high as 3×10^5 and

ρ values as high as 1400 have been reported.

C.G. Vayenas, et al, Electrochemical Activation of Catalysis, Kluwer/Plenum, New York, 2001; C.G. Vayenas and C.G. Koutsodontis, J. Chem. Phys. 128 (2008) 182506

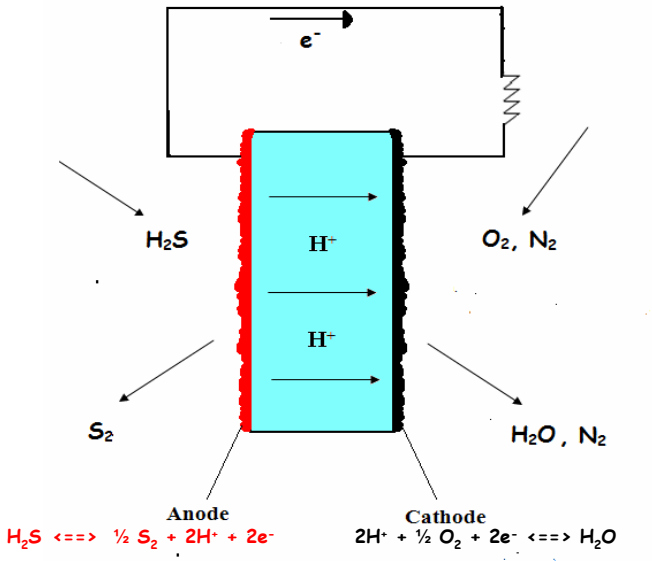
Chemical Cogeneration in Solid Oxide Fuel Cells



$$2\ CH_4 + 0.5\ O_2 <==> C_2H_4 + 2\ H_2O$$

Jiang et al, Science, 264 (1994) 1963; Guo et al, Catal. Today, 50 (1999) 109; Tagawa et al, Chem. Eng. Sci. 54 (1999) 1553

Chemical Cogeneration in a H^+ Fuel Cell



$$2\ H_2S + O_2 <==> S_2 + 2\ H_2O$$

D. Peterson and J.Winnick, J. Electrochem. Soc., 143 (1996) L55

Chemical Cogeneration Studies in SECRs (1980-)

Reactants	Products and byproducts	Catalysts
NH_3, O_2	NO, H_2O	Pt, $LiCoO_2$, $LaCoO_3$,
CH_4, O_2	C_2H_4,C_2H_6, CO, CO_2,H_2O	Fe,Au,Ag-Bi_2O_3,$La_xAl_yO_3$
CH_4,(H_2O),O_2	CO, H_2	Pt, Pd, Ni
CH_4, NH_3, O_2	HCN, CO, H_2O	Pt, Pt-Rh
C, O_2	CO, CO_2	Pt, Fe-C, TiC, ZrC, WC
H_2S, O_2	S_2, (H_2), SO_2, H_2O	Pt, Mo-Ni-S composites
CH_3OH, O_2	CH_2O, CO, CO_2	Ag
$C_6H_5C_2H_5$, O_2	$C_6H_5C_2H_3$, H_2O	Pt
C_4H_8, O_2	C_4H_6, H_2O	Pt
C_2H_6, O_2	C_2H_4, H_2O	Pt, Ag
C_3H_8, O_2	$CH_2CHCOOH$, H_2O	$MoV_{0.3}Te_{0.17}Nb_{0.12}O_3$
H_2S, CH_4, O_2	CS_2, H_2, CO_2, SO_2, H_2O	$La_{0.7}Sr_{0.3}VO_3$

Advantageous Characteristics of SECRs

Simultaneous production and separation of the desired compounds (e.g. $C_3H_8 \rightarrow C_3H_6 + H_2$). Also, impurities and poisons are avoided. No need for extensive purification.

Co-generation of electricity and valuable chemicals (e.g. $CH_4 + O_2 \rightarrow C_2H_4 + H_2O$ + Electricity).

The intrinsic catalytic activity can be dynamically modified (NEMCA). A large Λ value means that the electrochemical promotion can be achieved with a minimal consumption of electrical energy.

Disadvantages? Problems?

1) As opposed to traditional catalytic promotion, a different (new) reactor design is required:
   - ➔ high fixed cost
   - ➔ Immature testing (> 1000 hours)

2) Limited diversity in industry (for chemical cogeneration). Also, wires and electrodes are not welcome in chemical process industries.

3) The electrical conductivity of solid oxide fuel cells increases with temperature. But, at high temperatures, only small (inexpensive) molecules survive.

A detailed analysis is needed to determine the economic feasibility of a particular process

Example: Chemical cogeneration using methane as a fuel.

1) Methane to ethylene: $CH_4 + O_2 \rightarrow C_2H_4$ + electricity
2) Methane to synthesis gas: $CH_4 + O_2 \rightarrow CO + H_2$ + electricity
3) Methane fuel cell: $CH_4 + O_2 \rightarrow$ electricity (+ CO_2)

Studies of 1995 (Chiang et al, Energy & Fuels, 9, 794; Brousas et al, Ionics, 1, 328) indicated that, opposite to intuition, the methane fuel cell was economically the most attractive.

Ten years later, a new study [Hugill et al, Appl. Therm. Eng., 25 (2005) 1259] indicated that a plant cogenerating ethylene and electricity has a rather low profitability, **BUT**, CO_2 emissions are reduced significantly (environmental cost). Furthermore, a promising alternative for the oxidative coupling of methane was a mixed conducting (O^{2-}- e^-) reactor, which not only reduces CO_2 emissions, but also eliminates the oxygen plant.

The Outlook

Applications disregarded in the past, will be revisited with the possibility for further development:

a) Methane coupling or methane conversion to synthesis gas with O^{2-}, H^{+}, or mixed conductors.

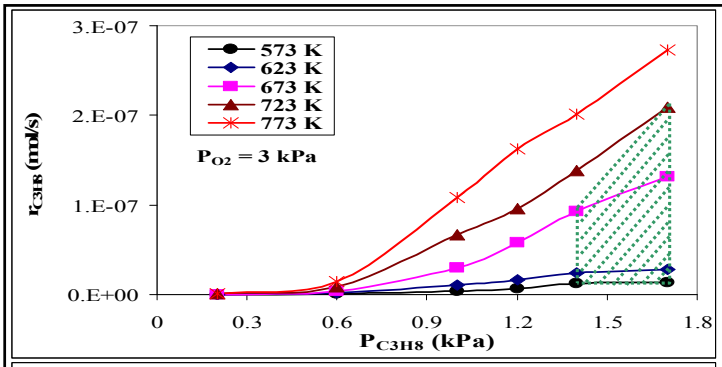
b) Conversion of alkanes into alkenes (e.g. C_3H_8 into C_3H_6) with simultaneous separation and production of pure H_2.

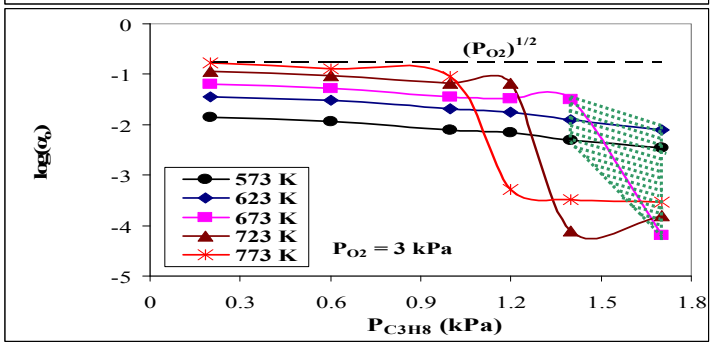
c) With the novel monolithic electropromoted reactor [S. Balomenou et al, Top. Catal. 44 (2007) 481], NEMCA is brought closer to utilization.

Conclusions

Catalytic studies in solid electrolyte cells have provided:
a) means and techniques to elucidate reaction mechanisms
b) means to improve the yield to the desired product.
c) alternatives to existing catalytic routes.

The activation energy to overcome the hurdles and bring SECRs into industrial practice will be the collaboration among researchers in the areas of heterogeneous catalysis, materials science and electrochemistry.





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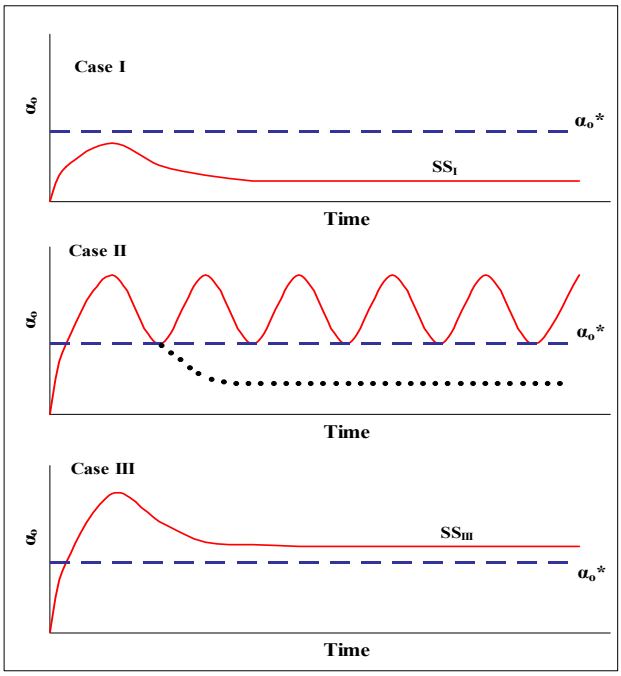

1) Mixed (O2-- e-) conductors for separation of O2 and N2 of the air and use of O2 for the partial oxidation of methane to synthesis gas. (Industry does not like electrodes).

2) Removal of hydrogen from hydrocarbon streams (with simultaneous hydrocarbon dehydrogenation) by using H+ EMRs.

3) The maturity of NEMCA makes EMRs more attractive:

a) There is no need for the reactant to be stoichiometrically transported through the S.E.

b) The single-chamber reactor design can be used.

c) A high reaction rate enhancement (ρ >> 1) can be considerably beneficial to industrial processes that curently operate at high pressures and temperatures (e.g. ammonia synthesis), because both P and T can be lowered without loss in the product yield.

d) With the "wireless" NEMCA [3] (electrochemical promotion when the catalyst is deposited on a S.E.) electrodes are not needed.

Either with the open or with the closed-circuit operation, EMR studies provided valuable information for the catalytic reaction mechanism, information that could not have been obtained otherwise.

Progress in materials science and solid state ionics is continuous; factors that inhibit scale up (e.g. materials cost), may be diminished.

And even if not, research in this particular field has provided the industrial world with a number of potential alternatives to existing catalytic routes.