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# Differential Electrochemical Mass Spectrometrie: applications in electrocatalysis and battery research

## DEMS

Die Elektrochemie macht Spass  
„electrochemistry is fun“

Helmut Baltruschat  
University of Bonn

Zenonas Jusys  
Ulm University

### Objective

- Learn for what problems DEMS is helpful
- Find the appropriate MS –vacuum-system
- Find the optimal cell type
- Learn to optimize the system to your particular needs

- **Historical**
- **The interface between electrolyte and vacuum**
- **The Vacuum System**
- **Cell Types**
  - *The Conventional Cell for DEMS*
  - *A Cell Allowing the Use of Massive Electrodes: The Thin Layer Cell*
  - *The Dual Thin Layer Cell for Continuous Flow Through of Electrolyte*
- **Calibration**
- **Factors Influencing the Detectability of a Species**
- **Examples**
  - *Oxidation of Small Organic Molecules*
  - *Characterization of Organic Adsorbates*
  - *Aprotic electrolytes*
- **special cell types**
- **Combination with devices (fuel cells, batteries)**
- **Combination of DEMS with other methods**
  - *EQCM*
  - *ESI-MS*
  - *FTIRS*
- **New developments**
  - *ILs in vacuum*
  - *ICP-MS*
  - *Membrane chip*

- Bruckenstein, S., Rao, R. and J. Gadde (1971). "Use of a Porous Electrode for in Situ Mass Spectrometric Determination of Volatile Electrode Reaction Products." J. Am. Chem. Soc. **93**: 793.
- Bruckenstein, S. and J. Comeau (1974). "Electrochemical mass spectrometry Part 1. - preliminary studies of propane oxidation on platinum." Faraday Discuss. Chem. Soc. **56**: 285.

**Gaseous Products formed at a porous gas diffusion electrode were collected in vacuum and then analysed by MS**

**==> signal proportional to faradaic charge**

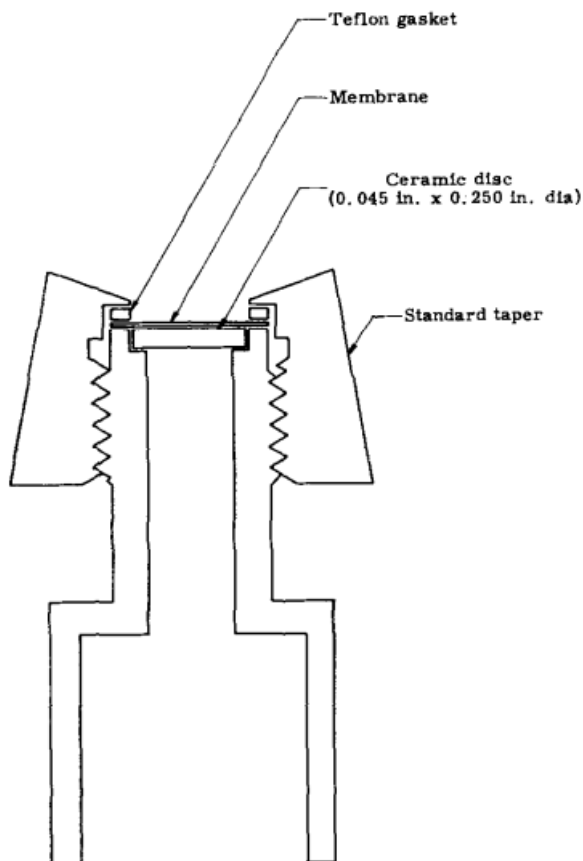
- Wolter, O. and J. Heitbaum (1984). "Differential Electrochemical Mass Spectroscopy (DEMS) - a new method for the study of electrode processes." Ber. Bunsenges. Phys. Chem. **88**: 2-6.
- Wolter, O. and J. Heitbaum (1984). "The adsorption of CO on a porous Pt-electrode in sulfuric acid studied by DEMS." Ber. Bunsenges. Phys. Chem. **88**: 6-10.
- **Gaseous products were analysed continuously *on line* in a differentially pumped MS**
- **==> signal proportional to faradic current (differentiated charge)**

→ **DEMS**

# Historical development: MIMS → EMS → DEMS

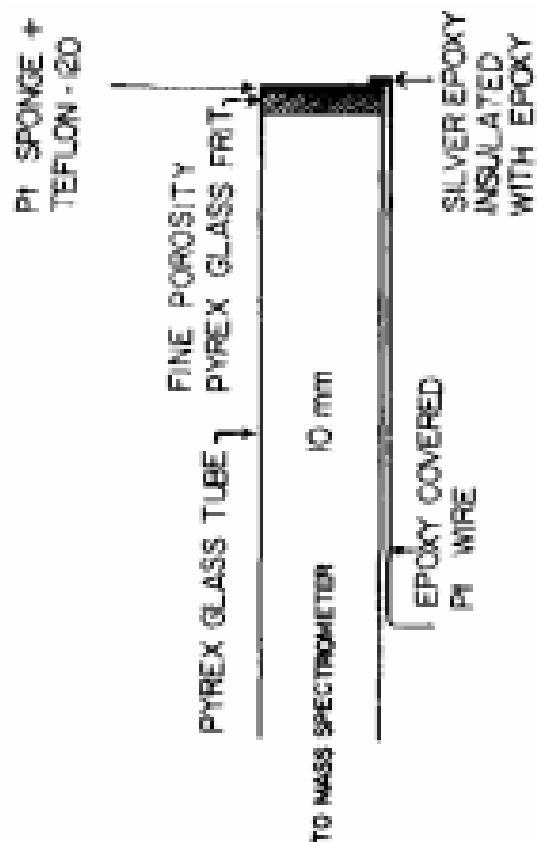


## MIMS



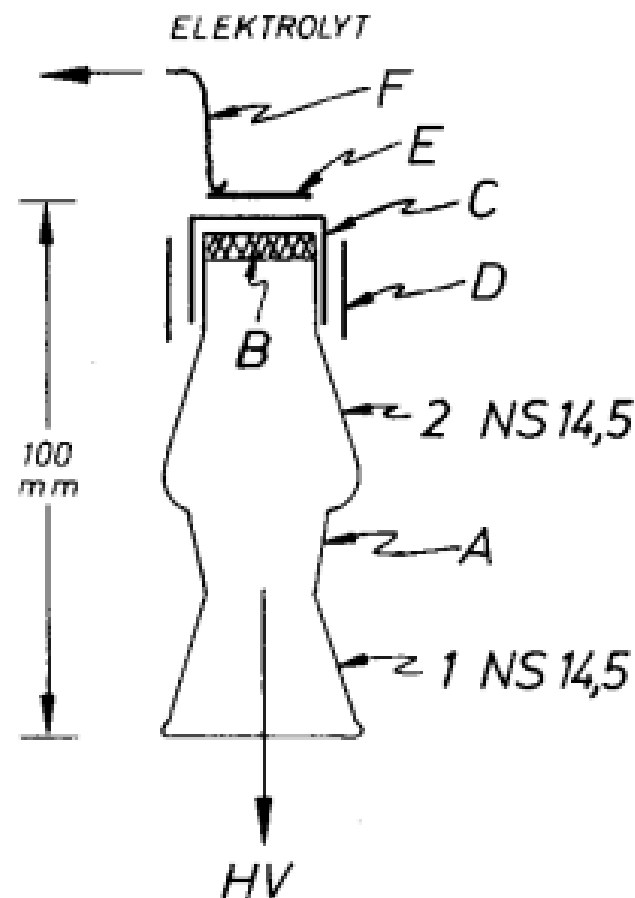
G. Hoch, B. Kok,  
Arch. Biochem. Biophys.  
101 (1963) 160-170

## EMS



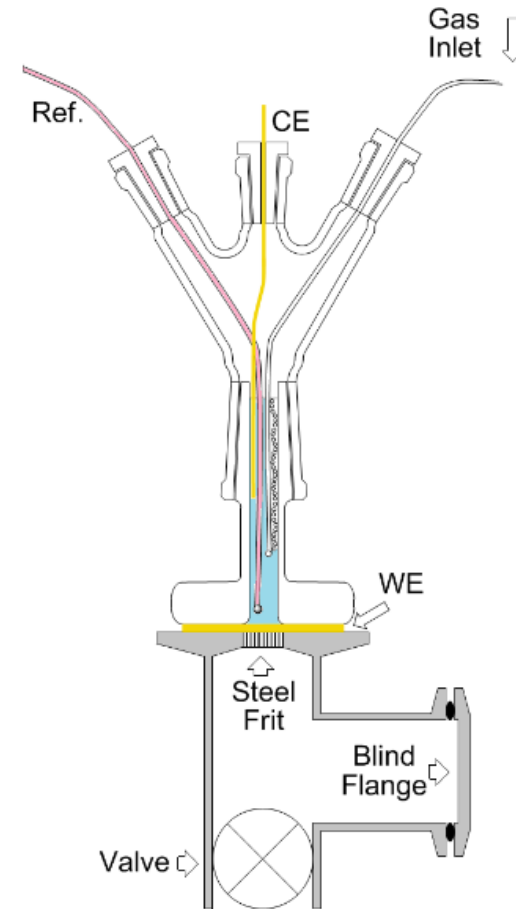
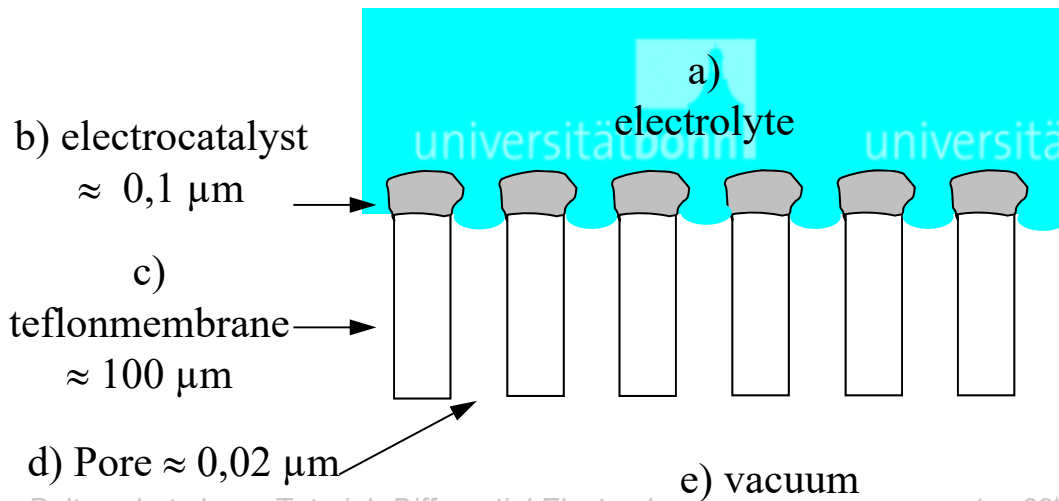
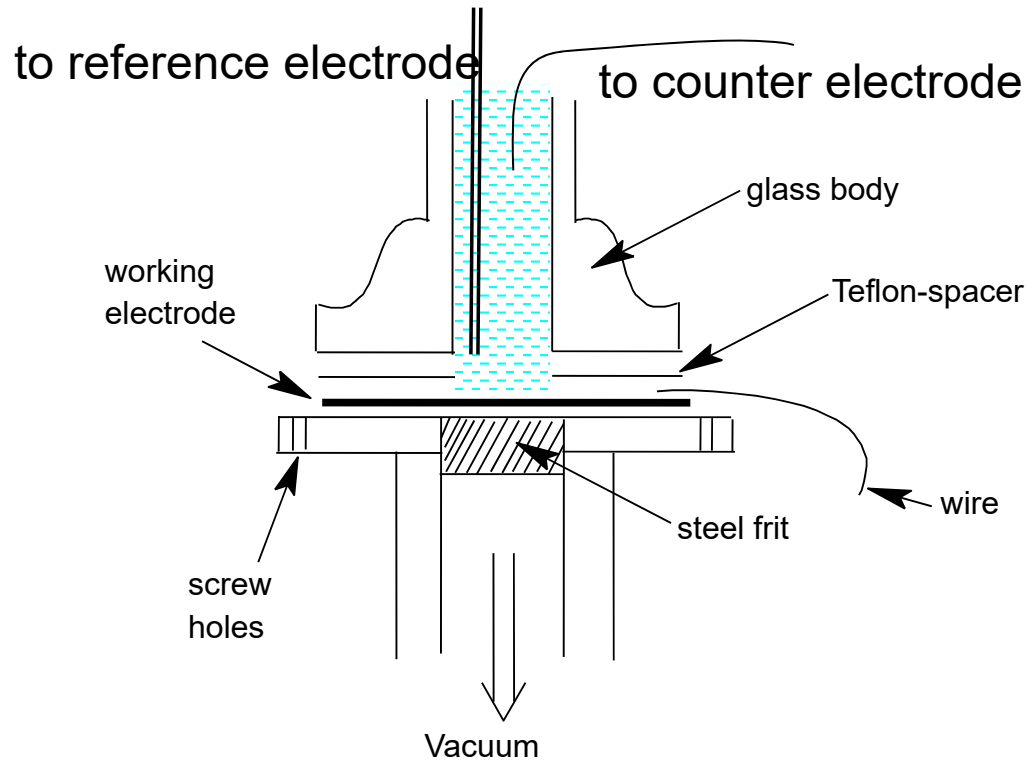
R.R. Gade, S. Bruckenstein,  
J. Am. Chem. Soc.  
93 (1971) 793-794

## DEMS



O. Wolter, J. Heitbaum,  
Ber. Bunsenges. Phys. Chem.  
88 (1984) 2-6

# The principle (example: „classical“ cell)



volatile products are formed at the electrode, diffuse to the electrolyte/gas interface, then evaporate into the vacuum

## Teflon membrane:

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interface between electrolyte (1 bar) and high vacuum( <math>10^{-4}</math> mbar)

requirements:

- density, to keep the vacuum below  $10^{-3}$  mbar.
- hydrophobicity, to hold back the liquid,
- porosity, to ensure a sufficiently high sensitivity (difference to MIMS!),
- permeability, to enable a fast flow of molecules  
(and to avoid time consuming diffusion resistance or memory effects inside the membrane).

fast diffusion, if the pores of the membrane are free of electrolyte.

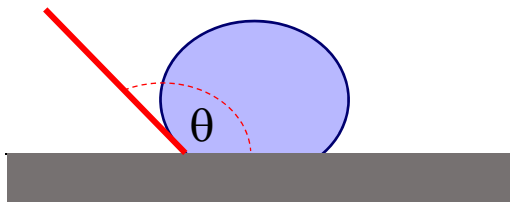
equation for a capillary:

$$r < - \frac{2\sigma \cos \theta}{p_0} \Rightarrow r < 0.8 \mu\text{m}$$

$\sigma$ : surface tension ( $72 \cdot 10^{-5} \text{ N cm}^{-1}$  for water)

$\theta$ : contact angle with the membrane ( $126^\circ$ )

$p_0$ : atmospheric pressure



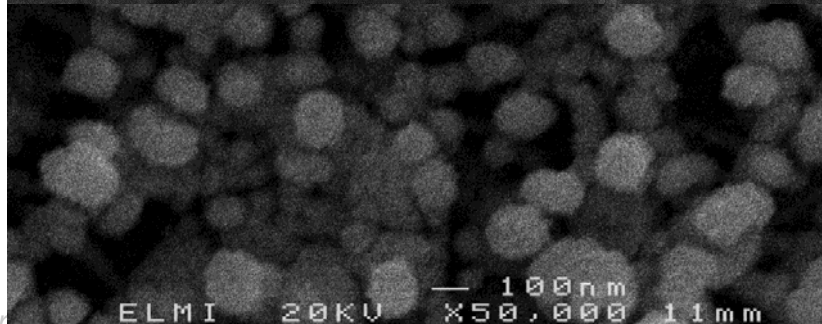
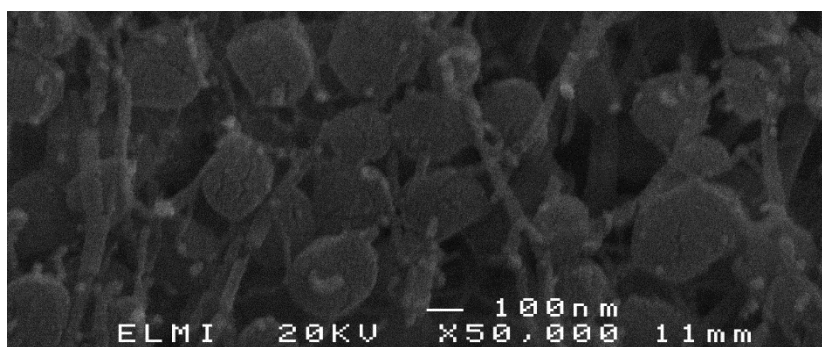
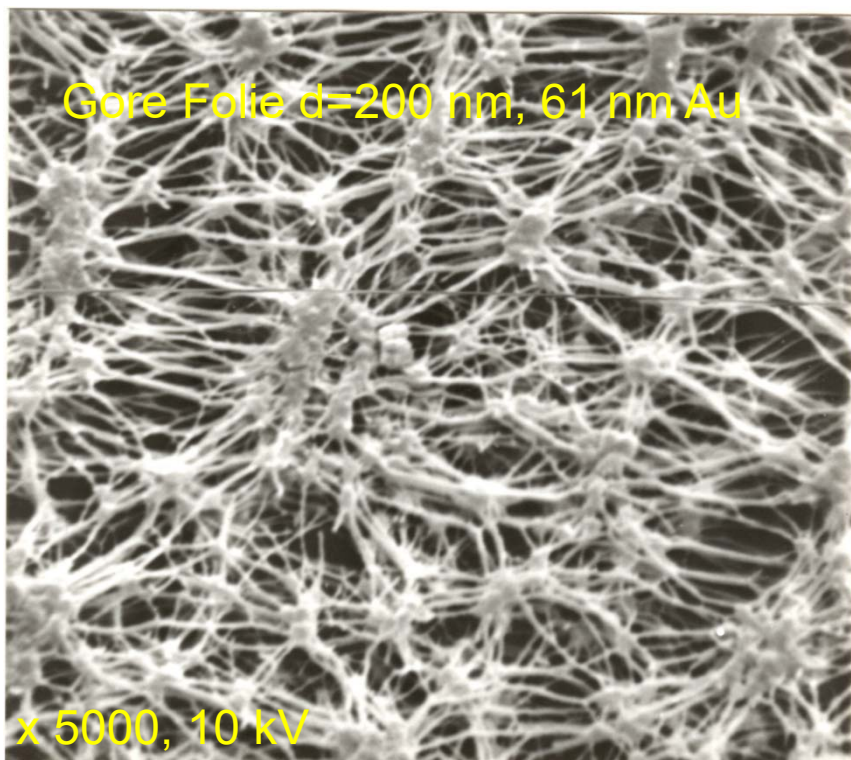
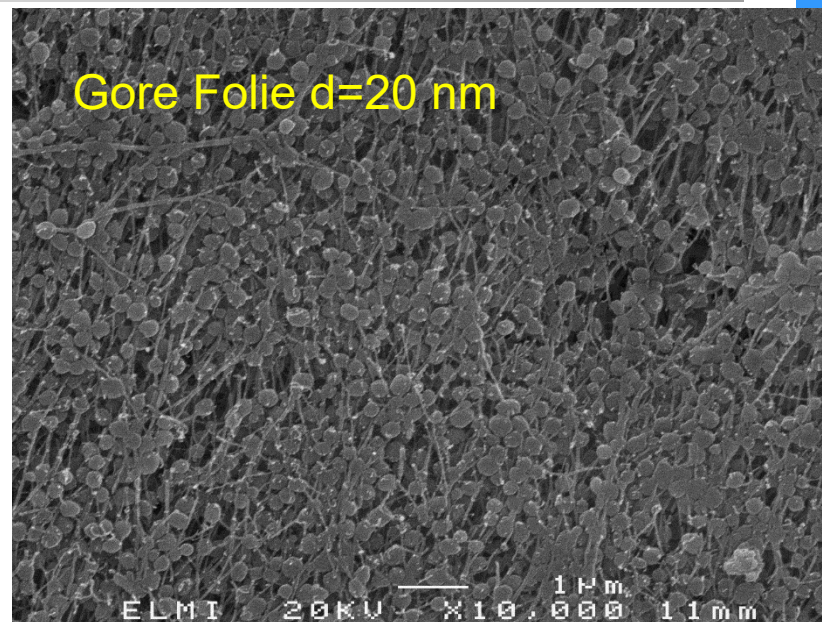
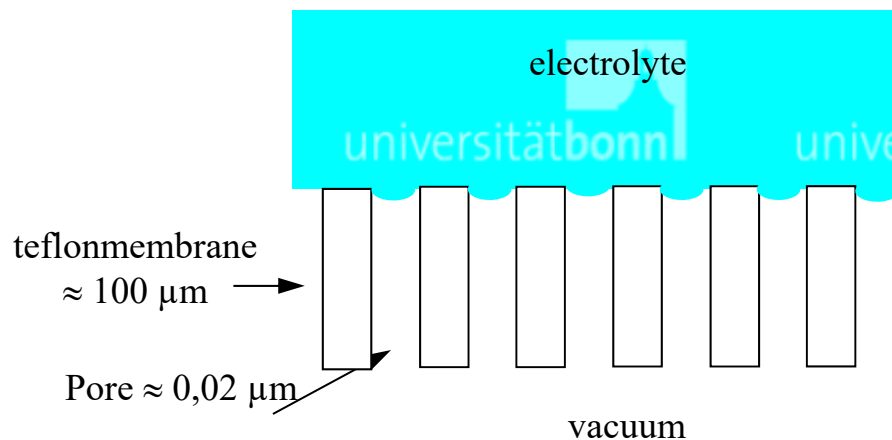
ethylene glycol:

$$\theta = 93^\circ, \sigma = 48 \cdot 10^{-5} \text{ N cm}^{-1} \Rightarrow r < 0.05 \mu\text{m}$$

practically usable:

water, propylene carbonate, DMSO, tetraglyme

Wolter, O.; Heitbaum, J., Differential Electrochemical Mass Spectroscopy (DEMS) - a new method for the study of electrode processes. *Ber. Bunsenges. Physikal. Chemie* **1984**, *88*, 2-6



## Teflon membrane: interface between electrolyte and HV ( $< 10^{-4}$ mbar)



molecular flow in the pores:

$$RT \cdot J = RT \cdot \frac{dn}{dt} = \frac{d(pV)}{dt} = 0.5 \cdot 3.1 \cdot 10^4 \frac{\text{cm}}{\text{s}} \cdot \frac{r}{l} \Delta p \cdot (1 \text{ cm}^2) = 0.41 \frac{\text{mbar} \cdot \text{l}}{\text{s}}$$

for  $r=0.02 \mu\text{m}$ ;  $l=75 \mu\text{m}$ ;  $\Delta p=100$  mbar; porosity 50%; area  $A=1 \text{ cm}^2$

vapour pressure of water: 100 mbar at  $40^\circ\text{C}$   
23 mbar at  $20^\circ\text{C}$

with a turbopump 200L/s:

$$RT \cdot J = \frac{d(pV)}{dt} = S \cdot p = 200 \text{ L s}^{-1} \cdot 10^{-3} \text{ mbar} = 0.2 \frac{\text{mbar} \cdot \text{L}}{\text{s}} \quad \text{flow for } A=0.5 \text{ cm}^2$$

the ion current  $I_i$  is proportional to the partial pressure  $p_i$ :

$$p_i = RT \cdot \frac{J_i}{S} \quad I_i = a \cdot p_i = a \cdot RT \cdot \frac{1}{S} J_i$$

$$I_i = K^0 \cdot J_i$$

$a$  and  $K^0$  contain all settings of the MS  
and the ionization probability of species  $i$

response time of the MS:  
sudden change of  $J_i$

$$V_0 \frac{dp_i}{dt} = RT \cdot J_i - p_i \cdot S$$

$$p_i = RT \cdot \frac{J_i}{S} \cdot (1 - e^{-t/\tau}) \quad \tau = \frac{V_0}{S}$$

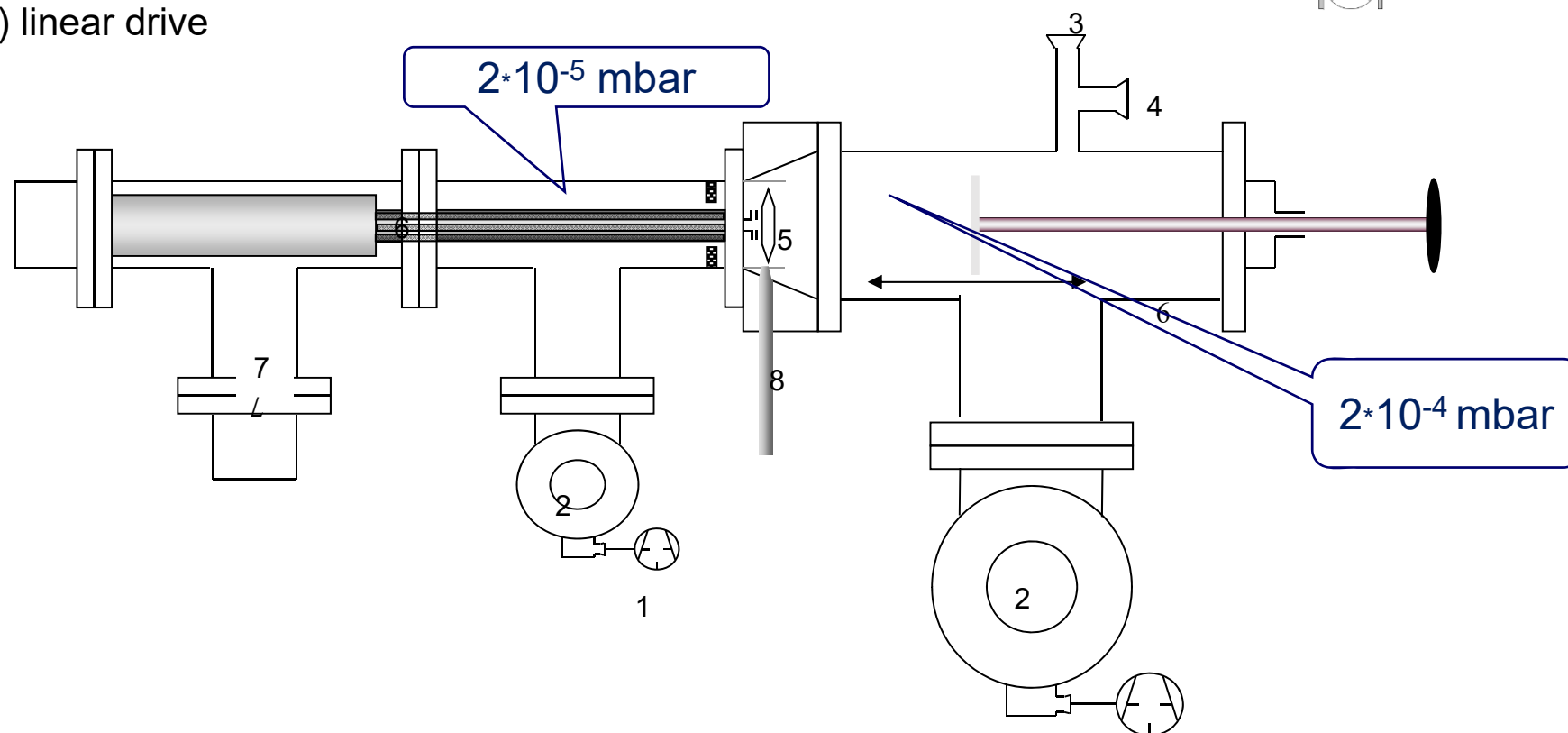
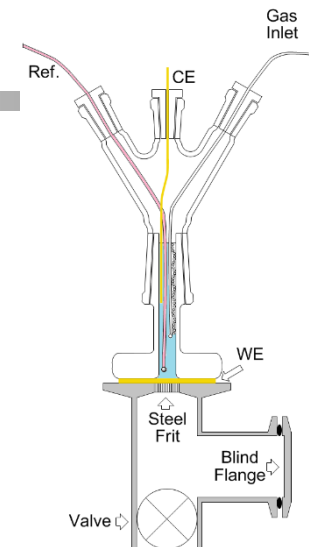
$$V_0 = 1 \text{ L} \implies \tau = 5 \text{ ms}$$

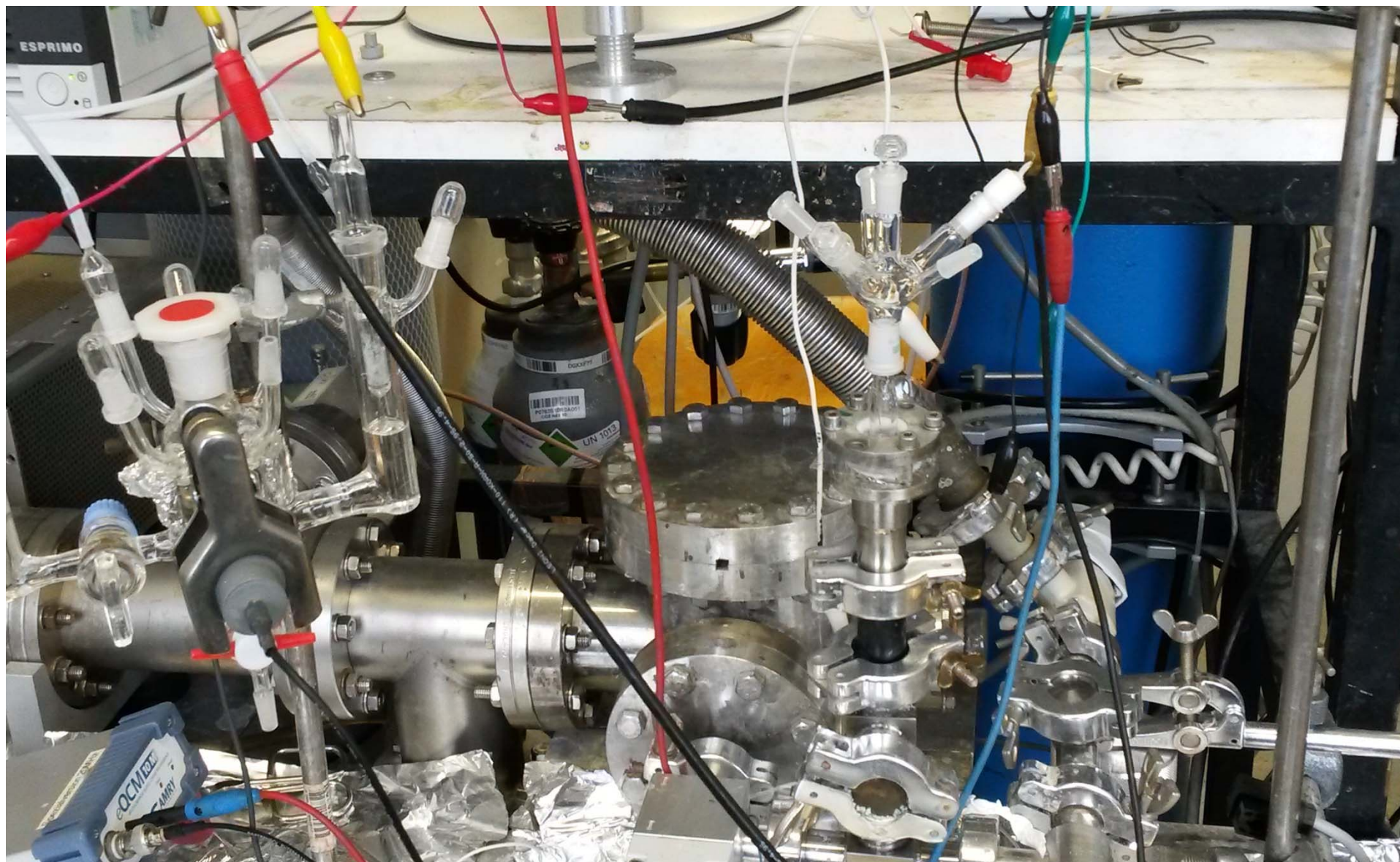


# The Vacuum System



- 1) rotary pumps
- 2) turbomolecular pumps
- 3) connection to the electrochemical cell
- 4) connection to the calibration leak
- 5) ion source (electron impact ionization)
- 6) quadrupol rods
- 7) secondary electron multiplier
- 8) direct inlet
- 9) linear drive





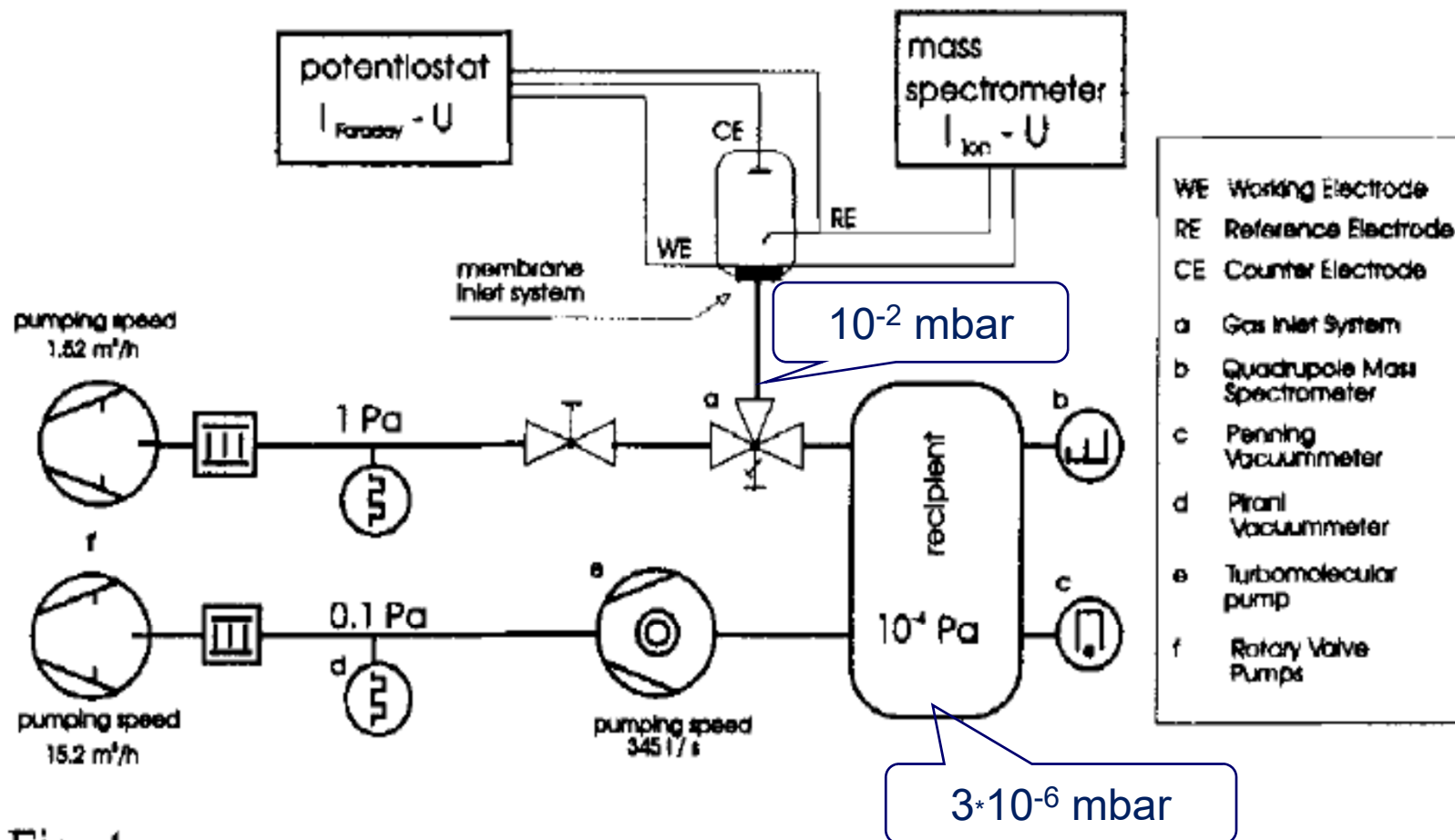
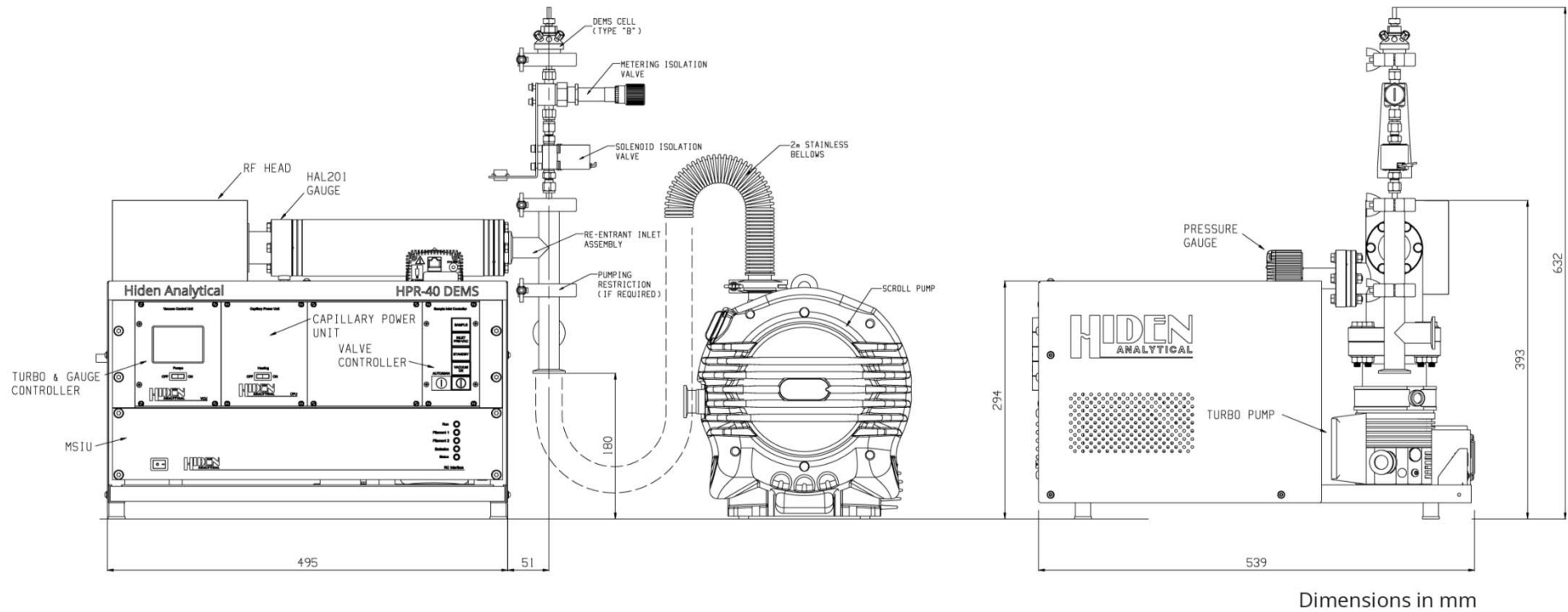


Fig. 1  
Schematic representation of the DEMS system

Ianniello, R.; Schmidt, V. M., A simplified DEMS set up for electrocatalytic studies of porous PtRu alloys. *Ber. Bunsengesellschaft Physikalische Chemie* **1995**, 99, (No.1), 83-86.

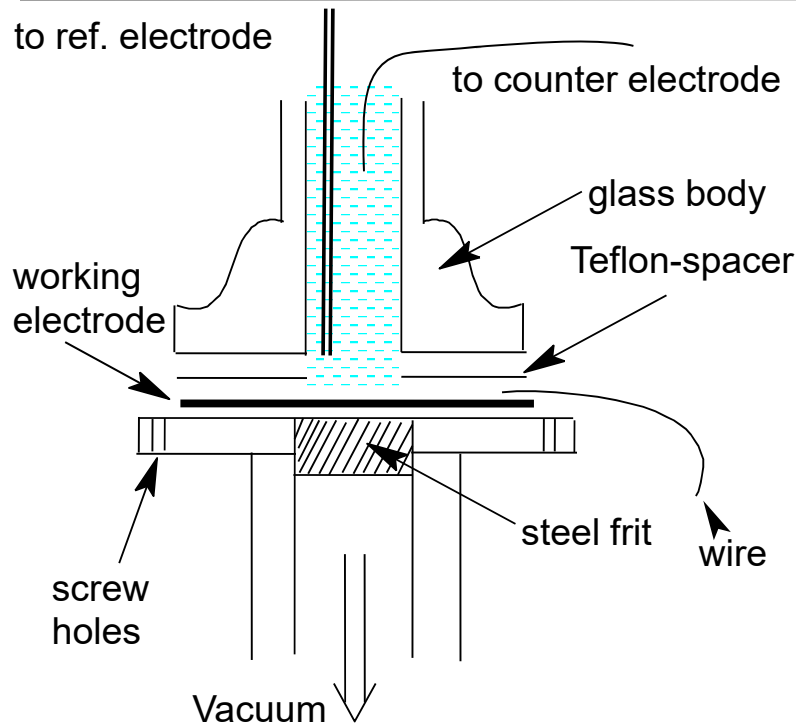
# The Vacuum System Commercial system (Hiden)



# The Vacuum System comparison of the pumping systems:

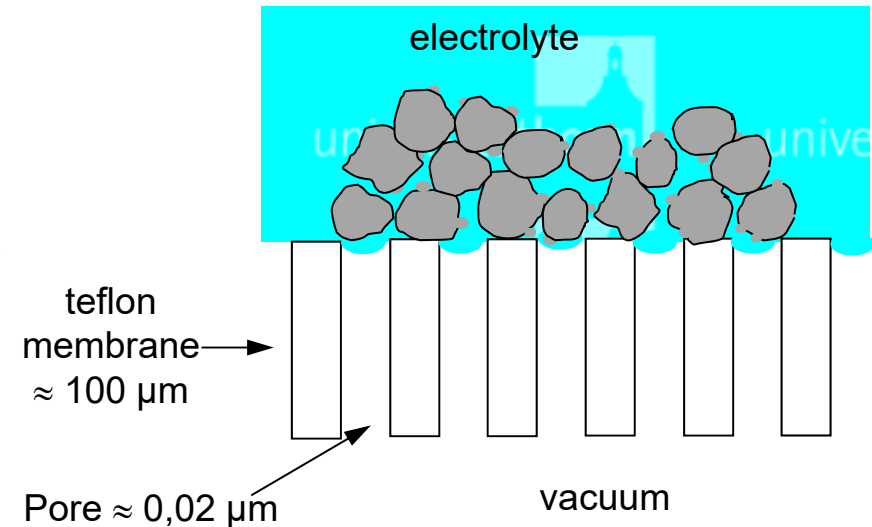
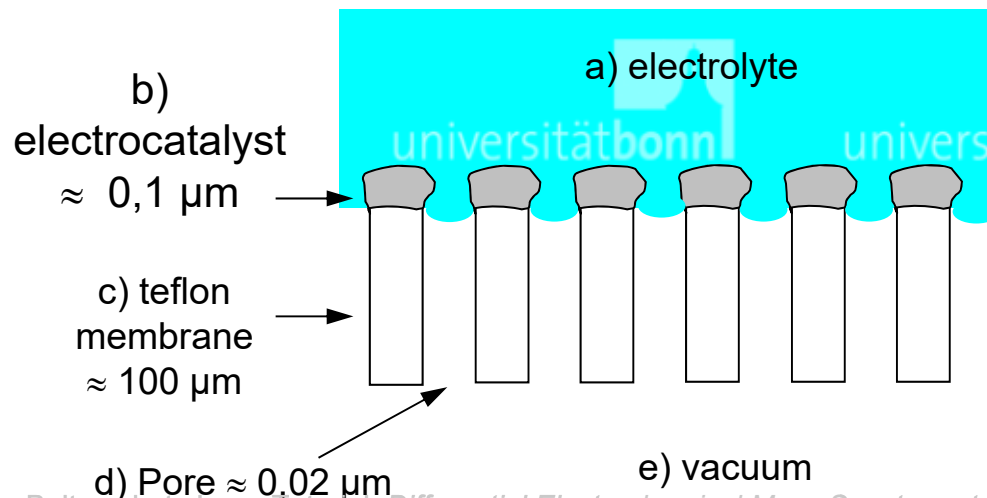


	<b>2 turbopumps</b>	<b>Rotary + turbo</b>	<b>Scroll + turbo</b>
1 <sup>st</sup> pumping stage	2*10 <sup>-4</sup> mbar ion source	10 <sup>-2</sup> mbar	0.1 ... 1 mbar ?
2 <sup>nd</sup> pumping stage	2*10 <sup>-5</sup> mbar	3*10 <sup>-6</sup> mbar ion source	? ion source
Advantages:	High sensitivity Less memory effects due to adsorption at chamber walls	Cheap “standard conditions” in the ion source	
disadvantages	High stress for the filaments (low lifetime)	Condensation, multilayer adsorption (cf. vap. pr. of naphthalene 0.1 mbar)	
	Secondary electrons ==> increased ionization probability		

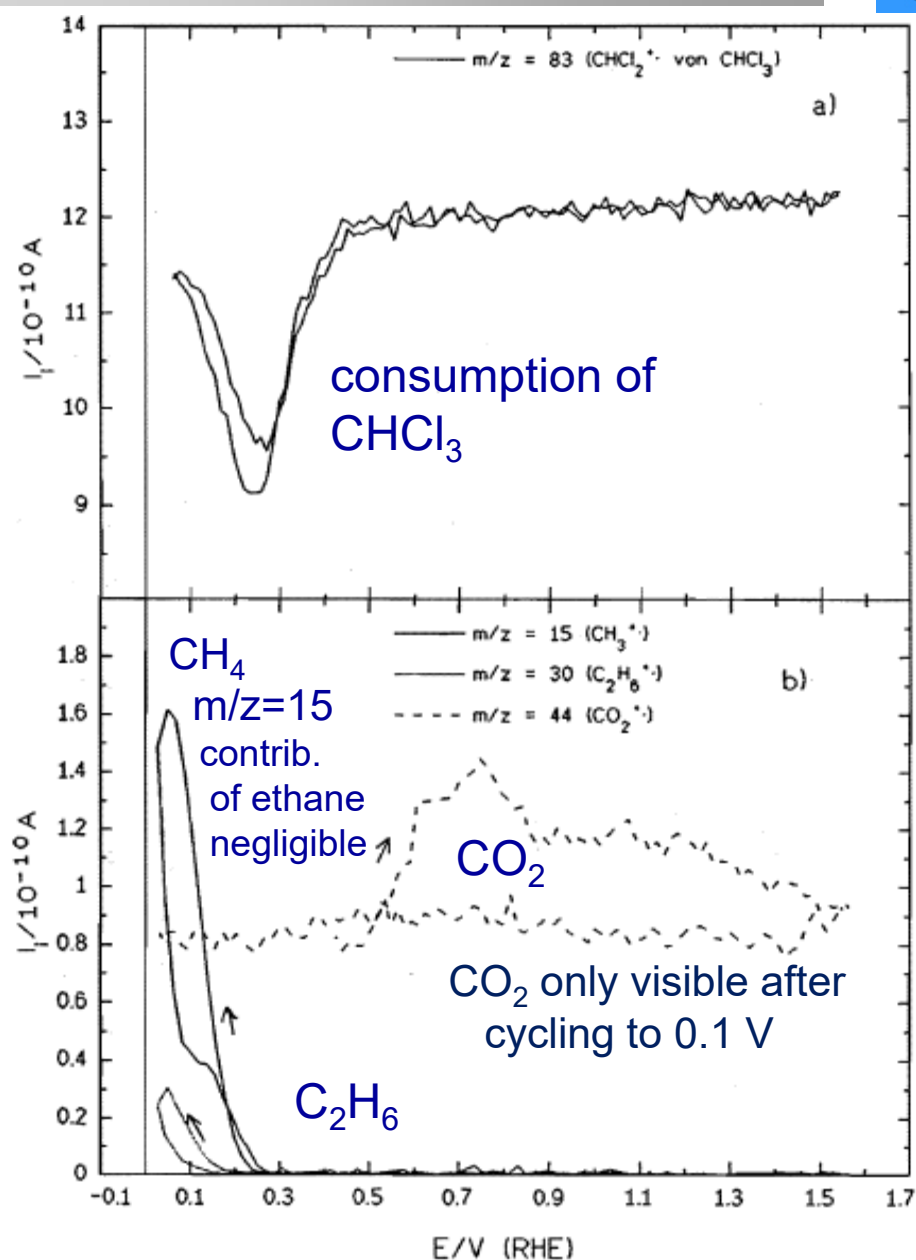
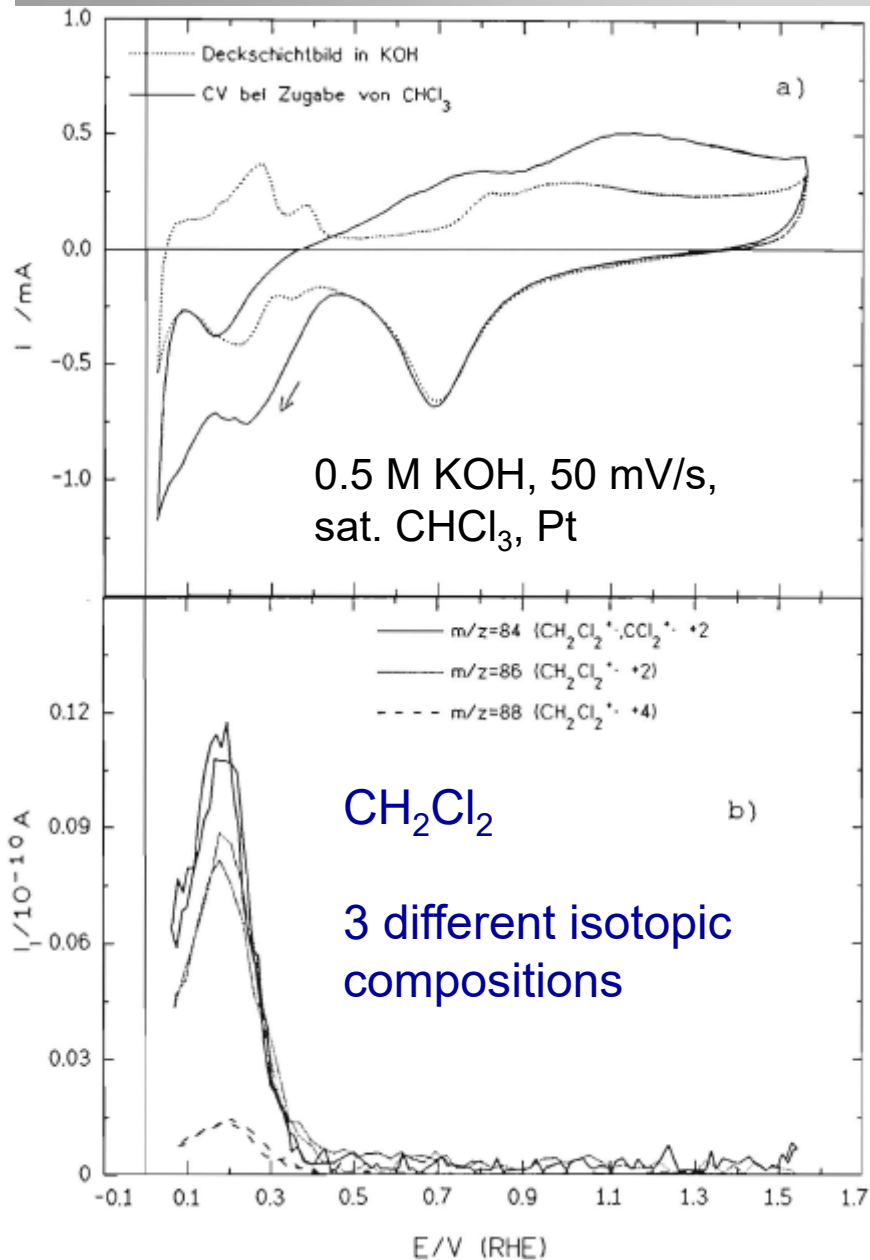


**Advantage:**  
 - very sensitive (RF ~10)

**Disadvantage:**  
 - no single crystals, no massive electrodes  
 - depletion of gaseous reactants due to evaporation  
 - thicker catalyst layers:  
     heterogeneous conc. profile of volatile reactants  
 - part of the products might diffuse away into the bulk of the electrolyte, others react further (dependent on convection)



# example: reduction of $\text{CHCl}_3$



# Calibration constants



above:

the ion current  $I_i$  is proportional to the partial pressure  $p_i$ :  $K^0$  contains all settings of the MS and the ionization probability of species  $i$

$$p_i = RT \cdot \frac{J_i}{S} \quad I_i = a \cdot p_i = a \cdot RT \cdot \frac{1}{S} J_i$$

ion current:  $I_i = K^0 \cdot J_i$       $J_i = N \cdot I_F / (z F)$       $I_i = K^0 N \cdot I_F / (z F) = K^* \cdot I_F / z$       $K^* = \frac{K^0 \cdot N}{F}$

transfer efficiency  $N = \frac{\text{formation rate}}{\text{amount of species penetrating the membrane}} = \frac{I_F / (z F)}{J_i} = \frac{I_F / (z F)}{I_i / K^0}$

For porous electrodes  $N$  depends on

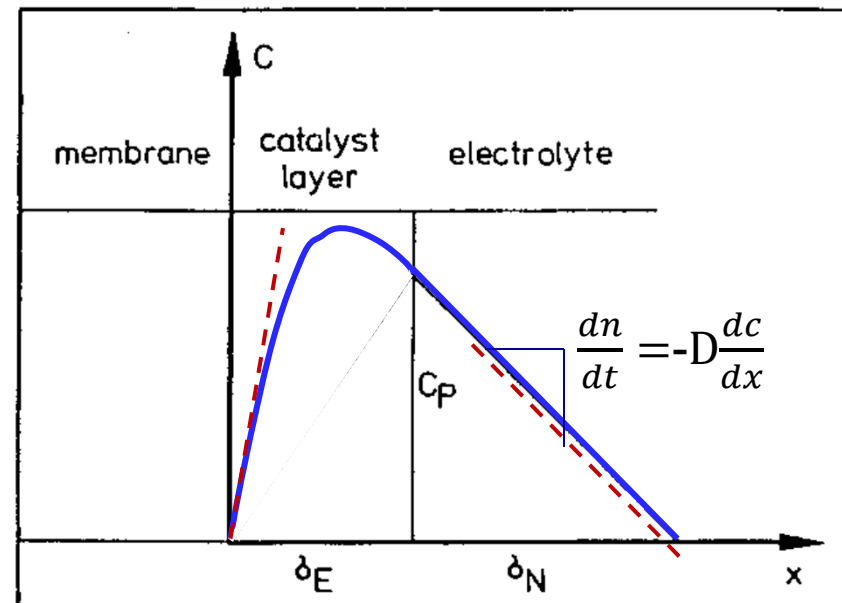
- thickness
- evaporation rate (volatility)
- convection (e.g. due to de-aeration)

$K^*$  depends on the MS-settings ( $K^0$ ) and the cell set-up ( $N$ ) and the species  $i$

$K^*$  can conveniently be determined using a reaction of known stoichiometry.

$K^*$  is then calculated from the ratio of the ionic current  $I_i$  to the Faradaic current  $I_F$

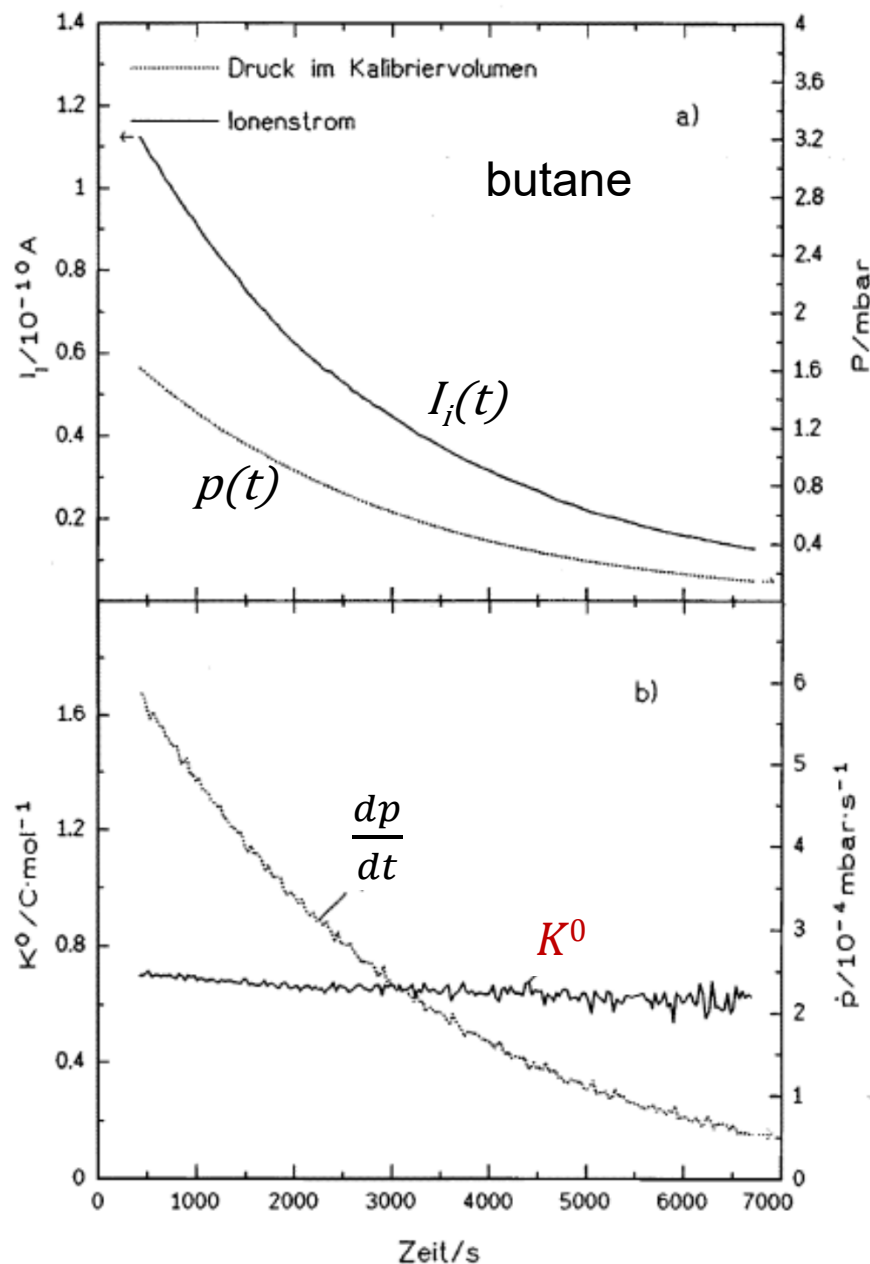
$$K^* = z \cdot \left| \frac{I_i}{I_F} \right|$$



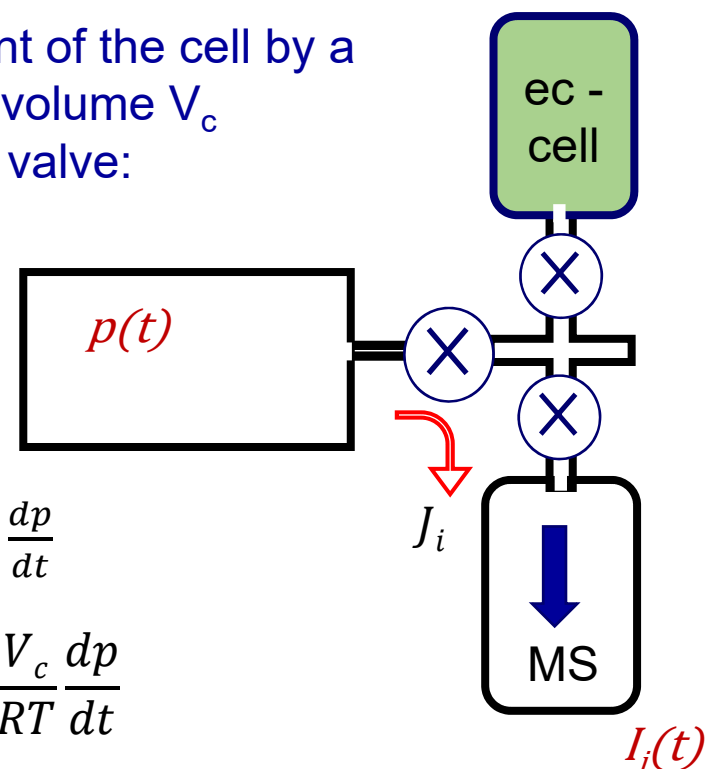
**Figure 4** Product concentration profile.  $\delta_E$ , Thickness of the electrode;  $\delta_N$ , diffusion layer thickness. adopted from Tegtmeier et al., *Ber. der Bunsenges. Physikal. Chemie* **1989**, 93, 201



## calibration: determination of $K^0$



replacement of the cell by a calibration volume  $V_c$   
+ needle valve:



$$p(t) \implies \frac{dp}{dt}$$

$$J_i = \frac{dn}{dt} = \frac{V_c}{RT} \frac{dp}{dt}$$

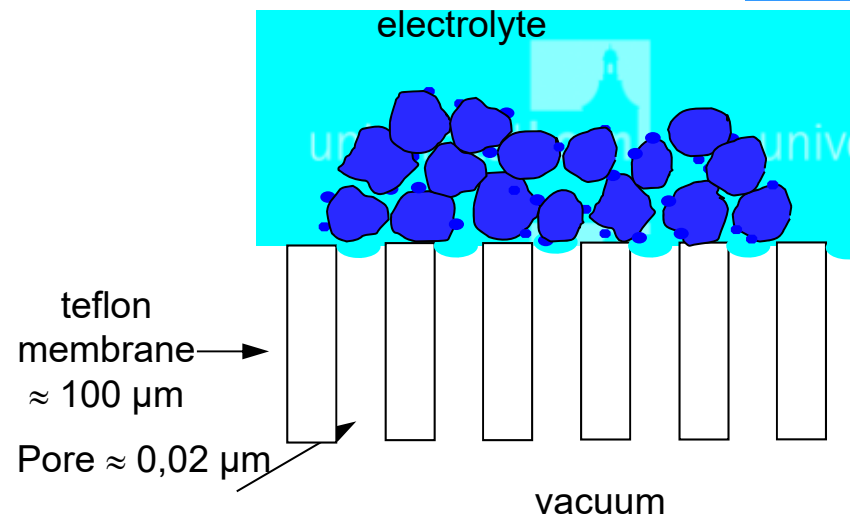
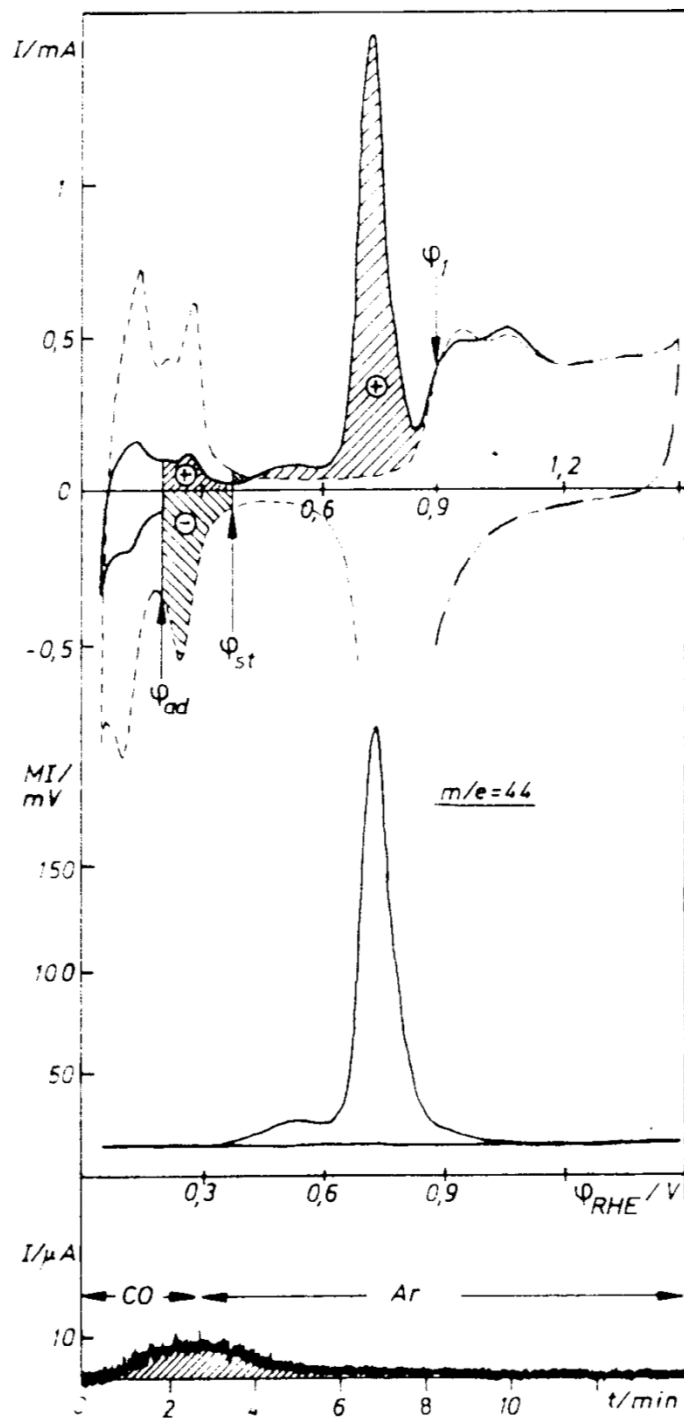
$$I_i = K^0 \cdot J_i = K^0 \cdot \frac{V_c}{RT} \frac{dp}{dt}$$

The calibration should be done under the same condition as the measurement itself.  
(The cell should be connected!)

Abb. 2.7:

Eichleckexperiment mit Butan. Die Ionenströme beziehen sich auf das Fragment mit  $m/z = 43$  ( $\text{C}_3\text{H}_7^{+\bullet}$ ).

# calibration for adsorbates: $\text{CO}_{\text{ad}} - \text{K}^*$



$$K^* = z \frac{I_i}{I_F} \quad \text{or} \quad K^* = z \frac{Q_i}{Q_F}$$

correlation of ox. charge and int. ion current of the MS:

Before and after the experiment the state of the electrode has to be the same.

- charge flow during adsorption (e.g. displacement of  $\text{H}_{\text{ads}}$ , change of DL composition) (\*)
- charge flow during oxidation sweep

(\*) cf. the determination of the pzc by the CO charge displacement by Feliu, Clavilier et al.

cf. also: Willsau, J.; Heitbaum, J., Analysis of adsorbed intermediates and determination of surface potential shifts by DEMS. *Electrochim. Acta* **1986**, 31, 943.

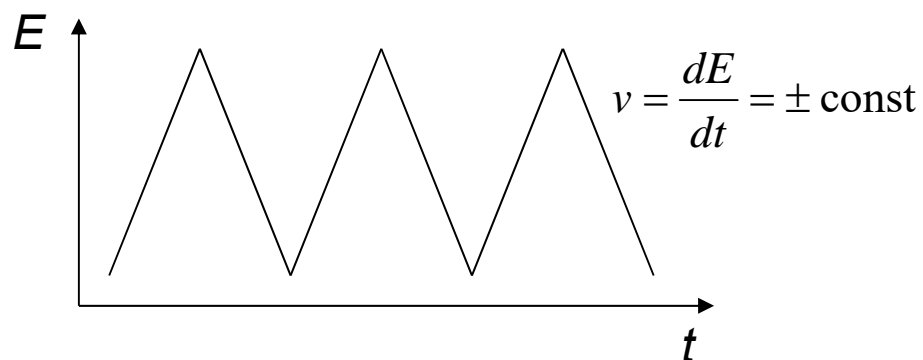
# Cyclic voltammetry – adsorption

## Adsorption :



$$\frac{\theta}{(1-\theta) \cdot c} = K = K_0 \cdot e^{zFE/RT} \quad \theta = \frac{K \cdot c}{1 + Kc}$$

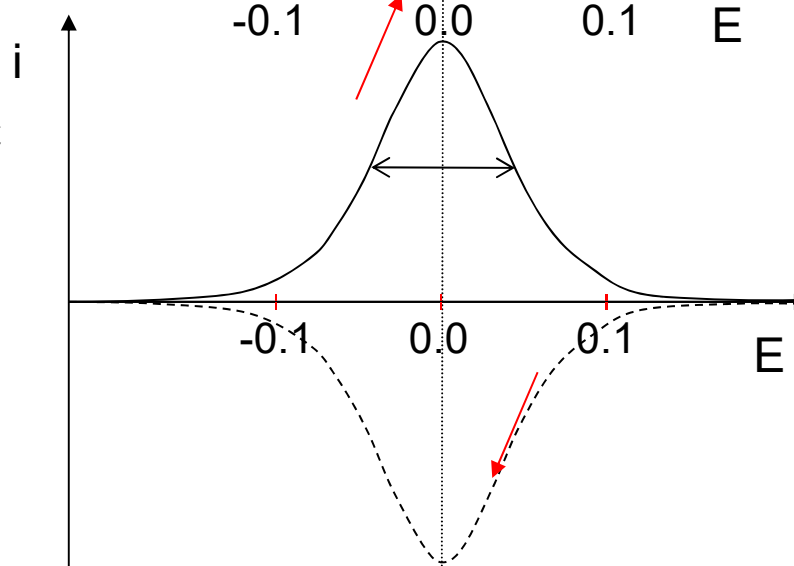
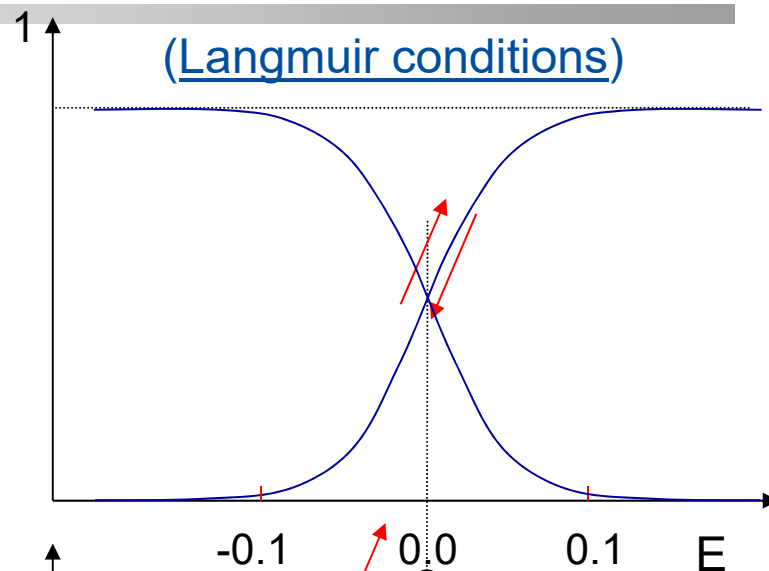
$$\theta = \frac{\Gamma}{\Gamma_{max}} \quad \Gamma: \text{surface conc.}$$



$$zF \cdot \Gamma_{max} = q_{max}$$

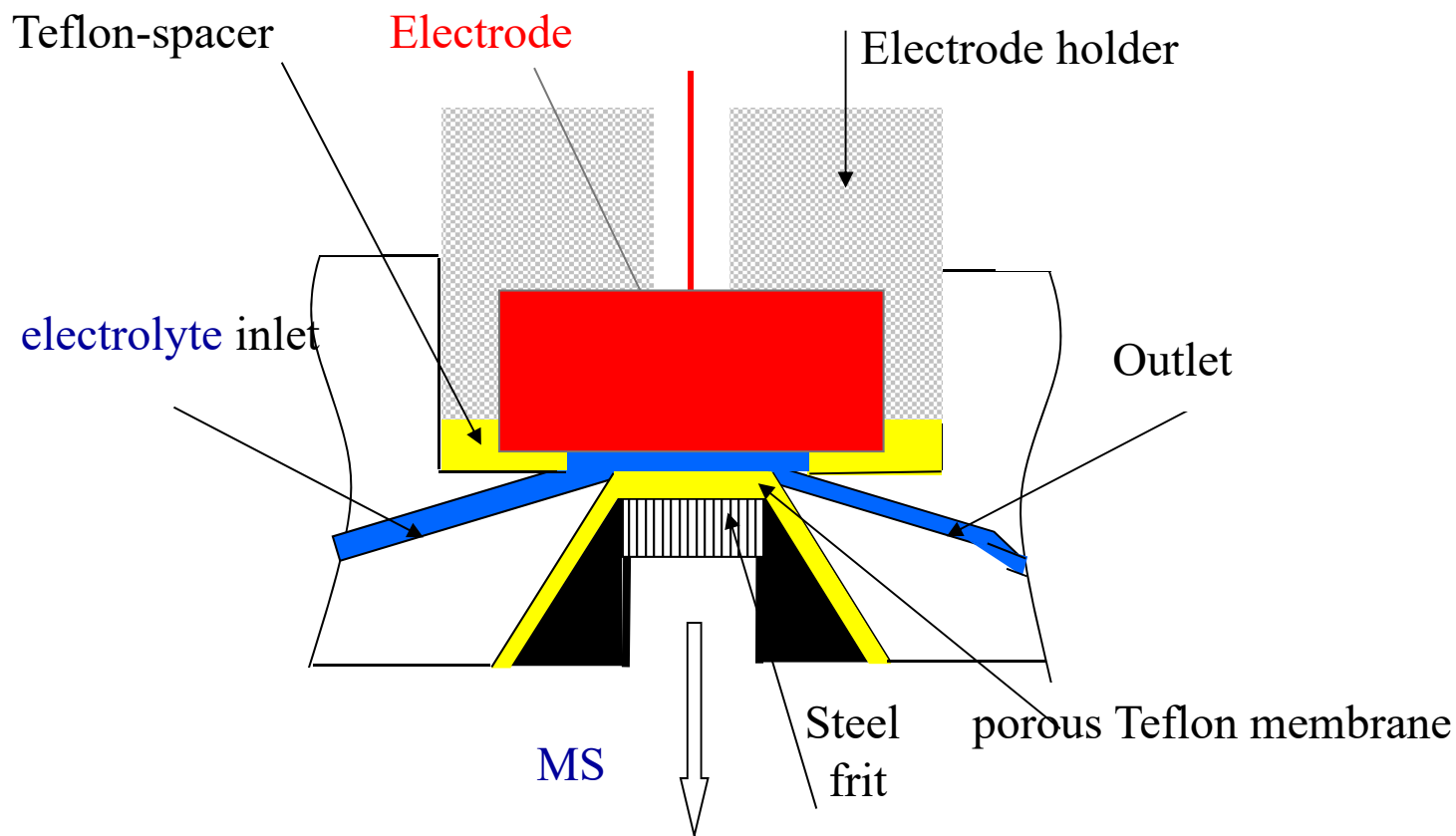
$$zF \cdot \Gamma(E) = q(E) \quad i = \frac{dq}{dt} = zF \cdot \frac{d\Gamma}{dE} \cdot \frac{dE}{dt}$$

$$F: \text{Faraday constant} \quad i = \frac{dq}{dt} = q_{max} \cdot v \cdot \frac{d\theta}{dE}$$



Peak position: energetics of adsorption  
(Stärke der WW mit dem Substrat)

Peak width: strength of interaction of  
adsorbed molecules

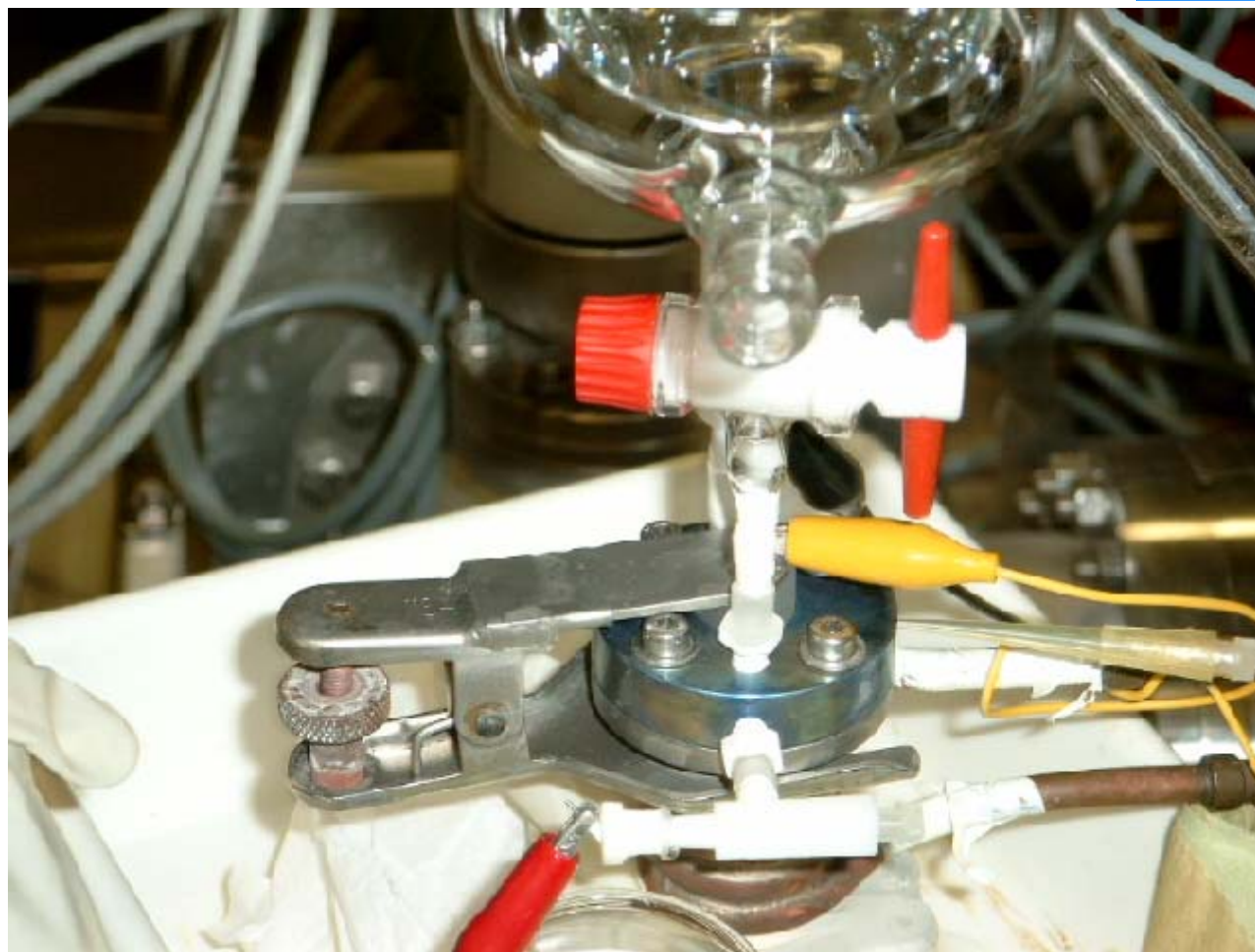


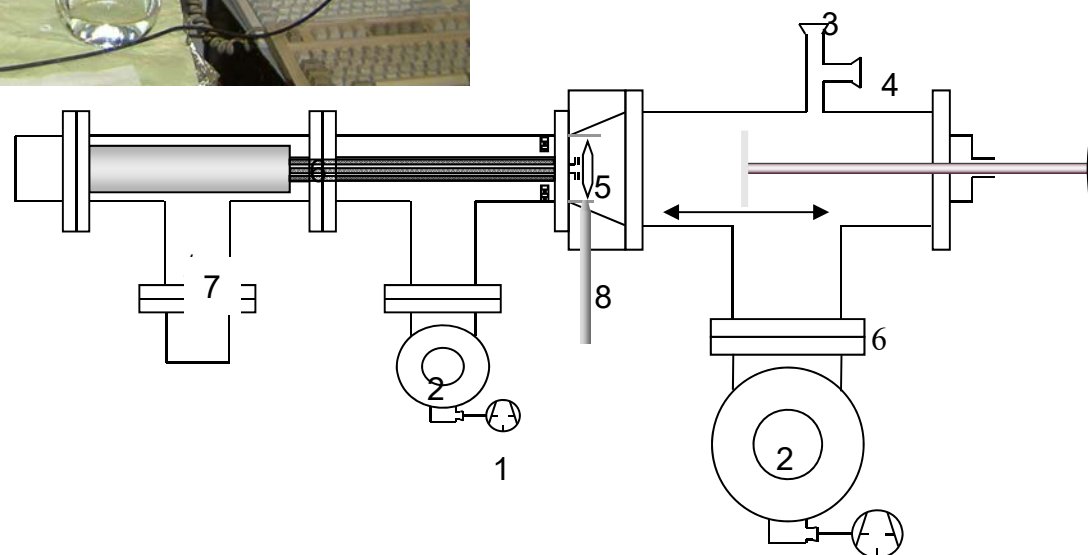
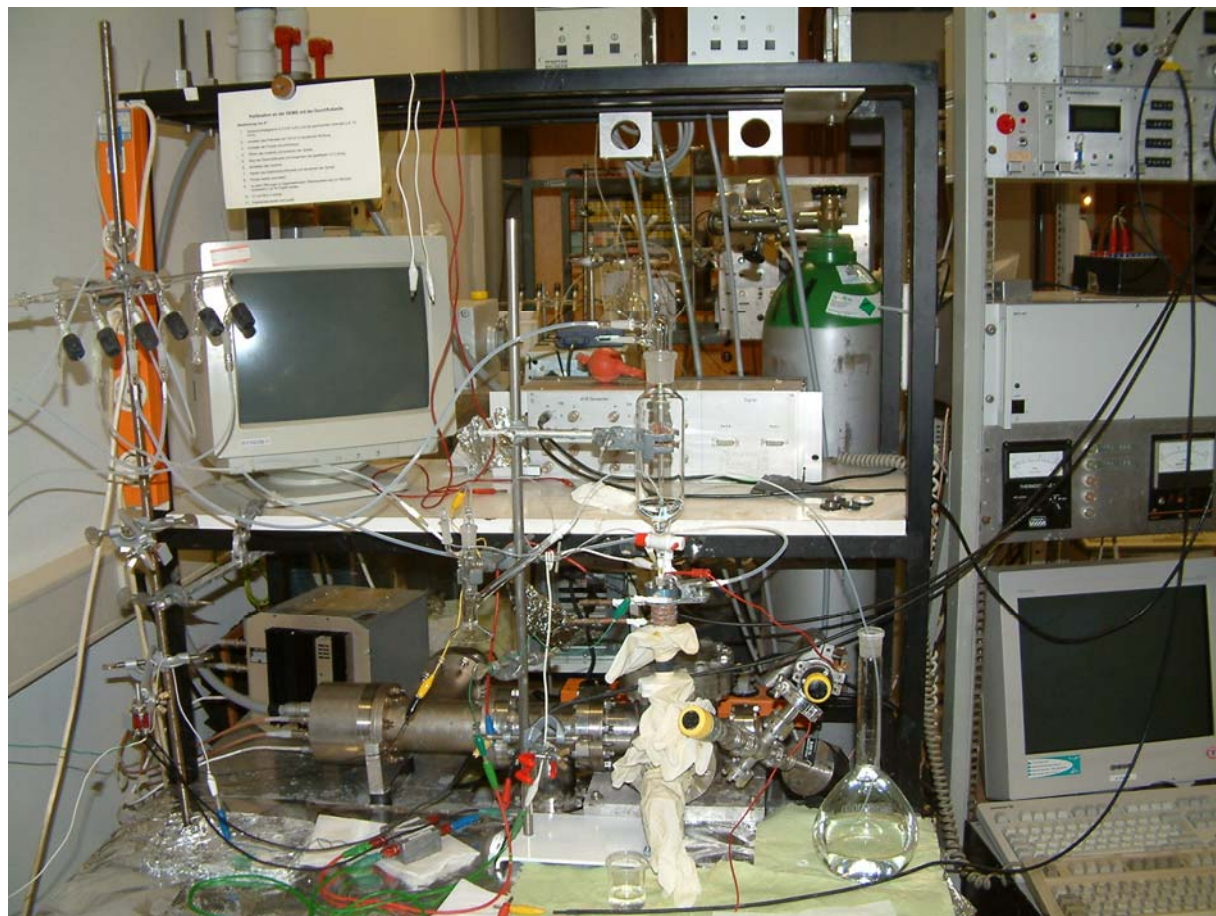
Sensitive for desorption experiments  
(transfer coefficient  $N \sim 0.9$ )  
Unsuitable for continuous reactions

Hartung, T. and H. Baltruschat (1990). *Langmuir* 6(No.5): 953-957.

*Thin layer electrodes*: A. T. Hubbard and F. C. Anson *ANAL. CHEM.* 36, 1964, 724

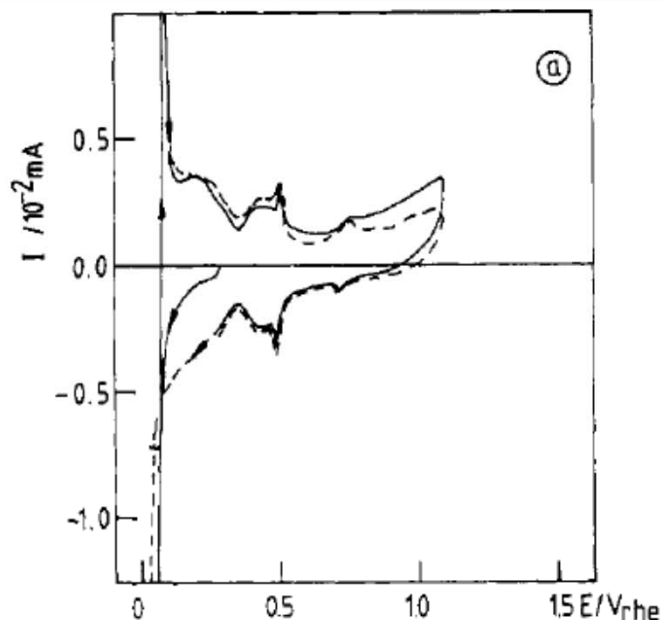
Baltruschat, Jusys Tutorial: *Differential Electrochemical Mass Spectrometry*. 69<sup>th</sup> Annual ISE Meeting, 2-7.09.2018, Bologna, Italy



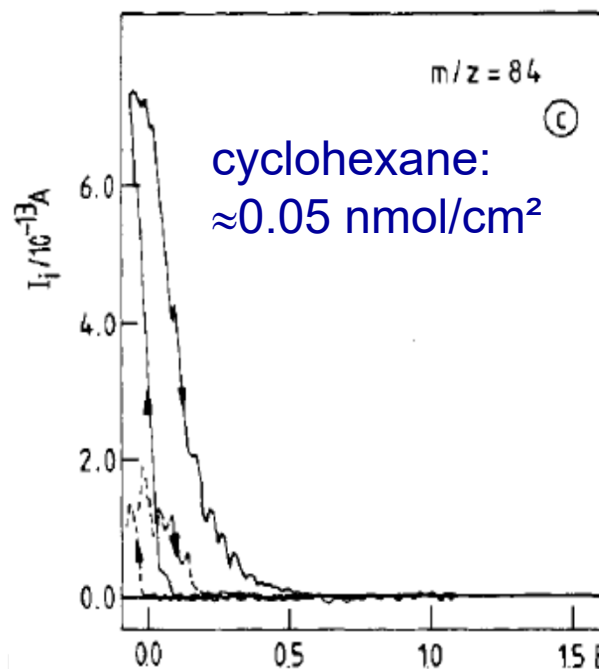
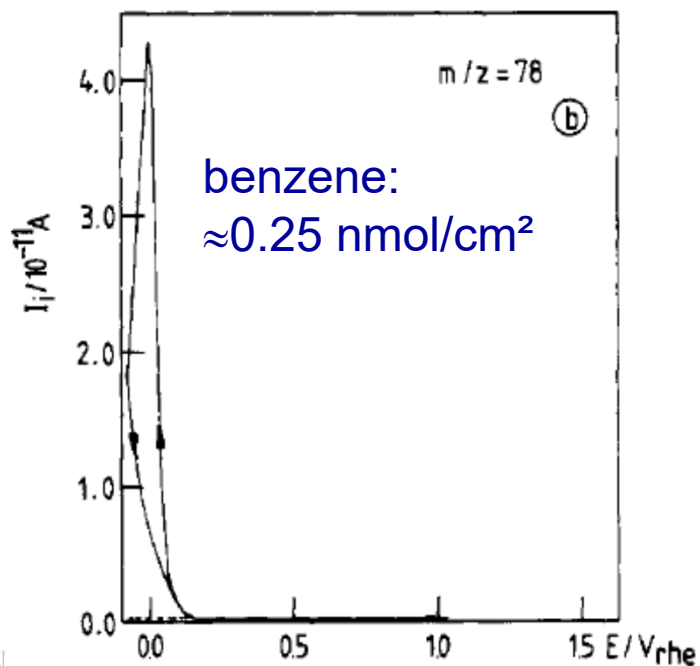


- 1) Rotationspumpe
- 2) Turbomolekular Pumpe
- 3) Anschluss der elektrochemischen Zelle
- 4) Anschluss Eichleck
- 5) Ionenquelle
- 6) Quadrupolstäbe
- 7) Elektronenvervielfacher
- 8) Direkteinlass

example      Electrodesorption of pre-adsorbed benzene from Pt(111)

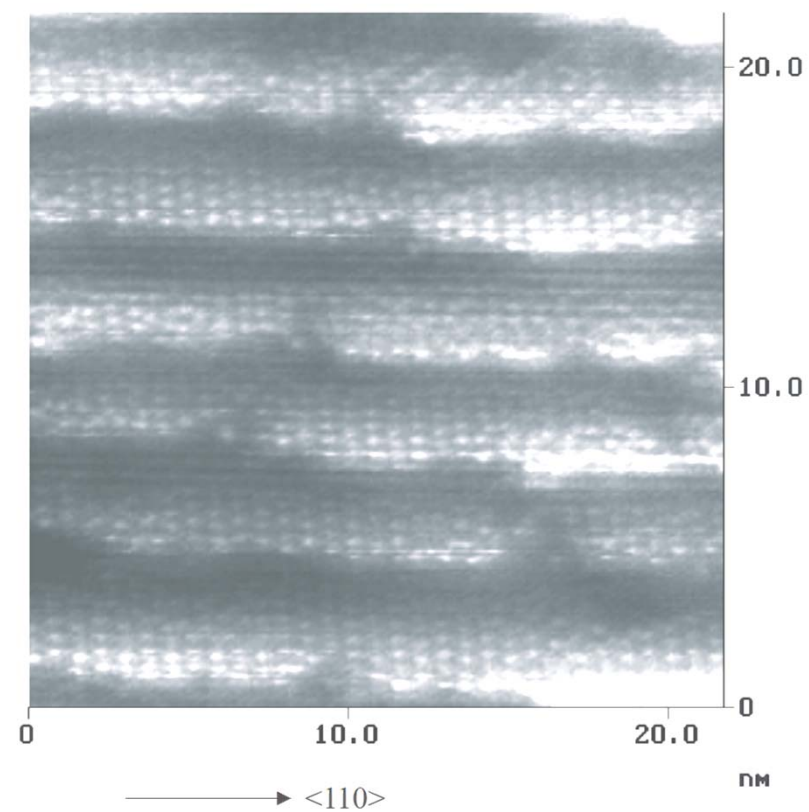


**Figure 2.** Electrodesorption of benzene from Pt(111) after adsorption from a  $2 \times 10^{-4}$  M benzene solution followed by electrolyte exchange with 0.05 M  $H_2SO_4$ ;  $E_{ads} = 0.2$  V;  $v = 12.5$  mV/s; cathodic potential limit  $-0.1$  V. Broken line: second sweep. (a) Cyclic voltammogram, (b) MSCV for benzene, (c) MSCV for cyclohexane.



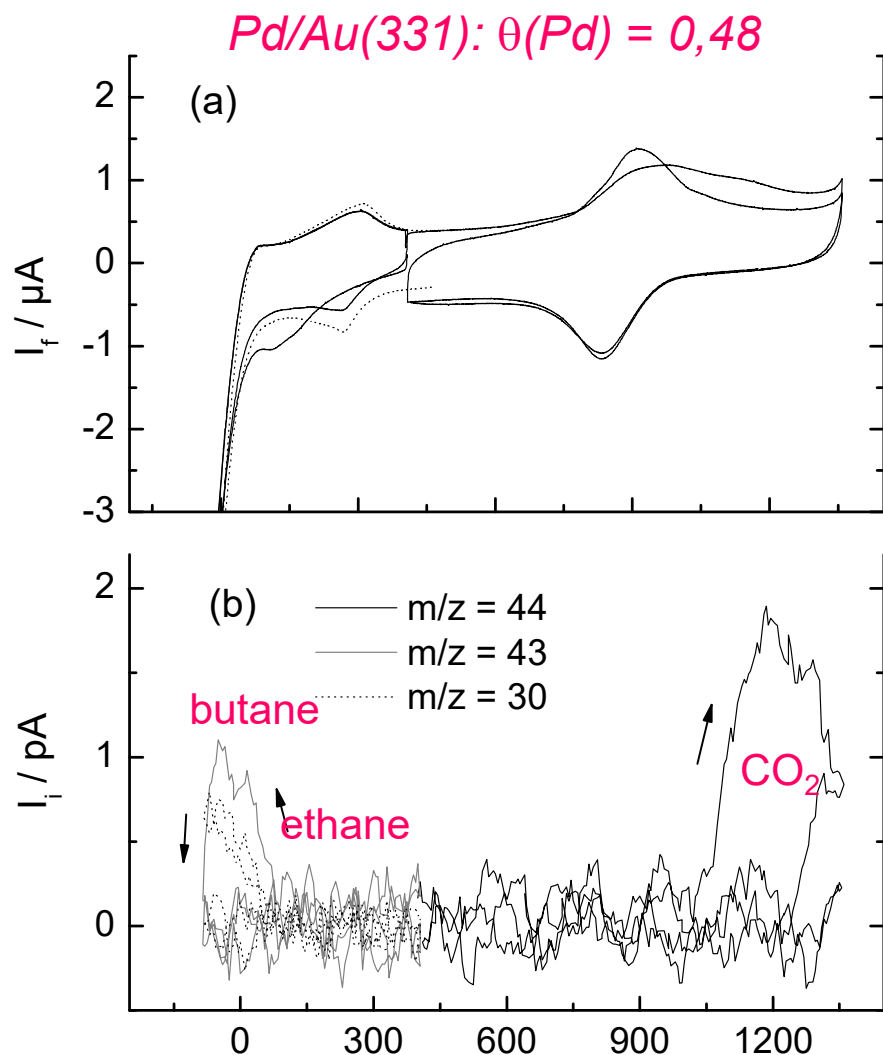
Pt(332), pc Pt:  
ratio reversed

Hartung, Schmiemann,  
Baltruschat, H., *Anal. Chem.*  
**1991**, 63, 44-48.

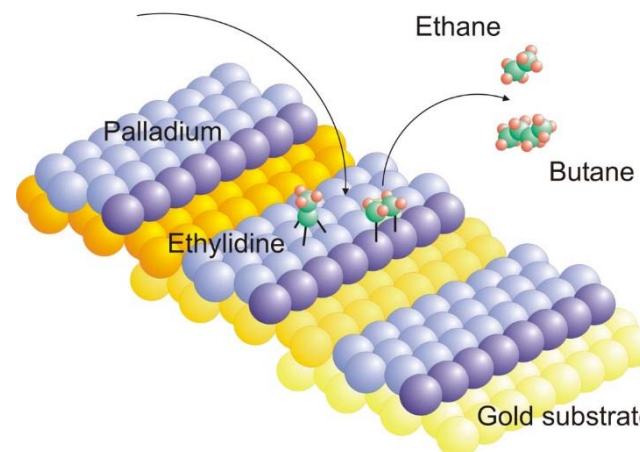
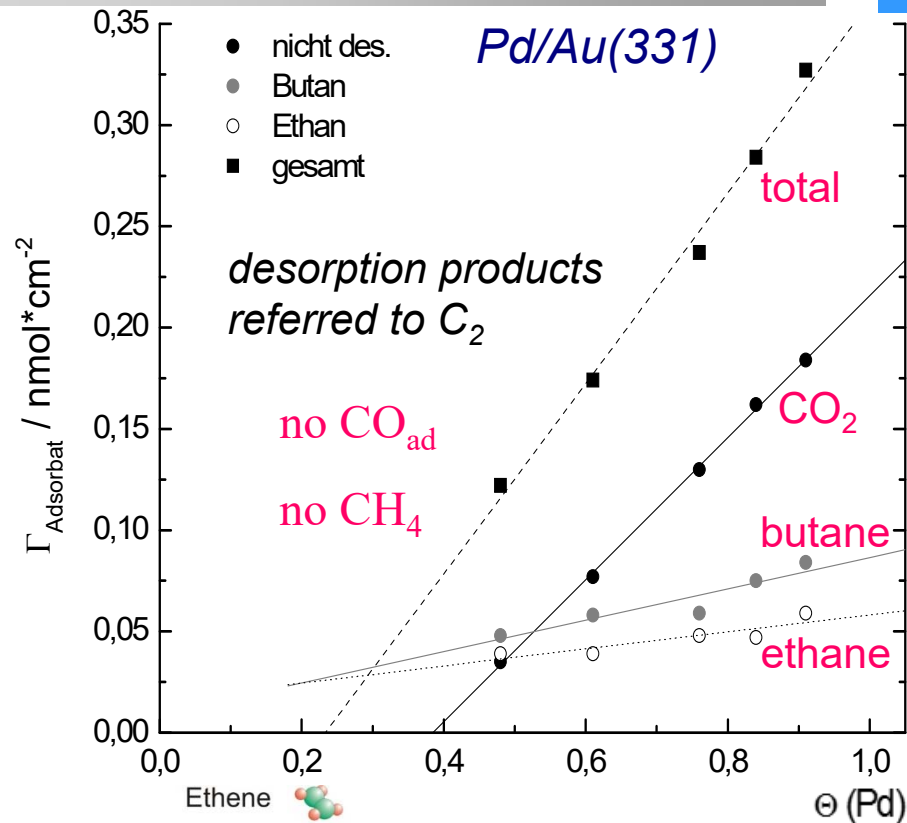




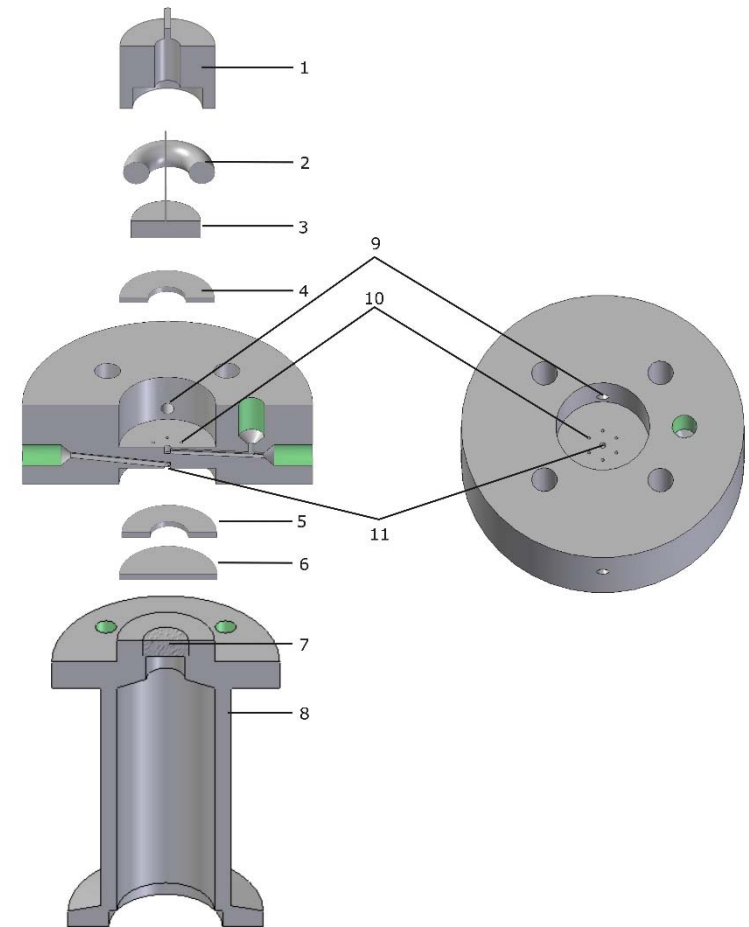
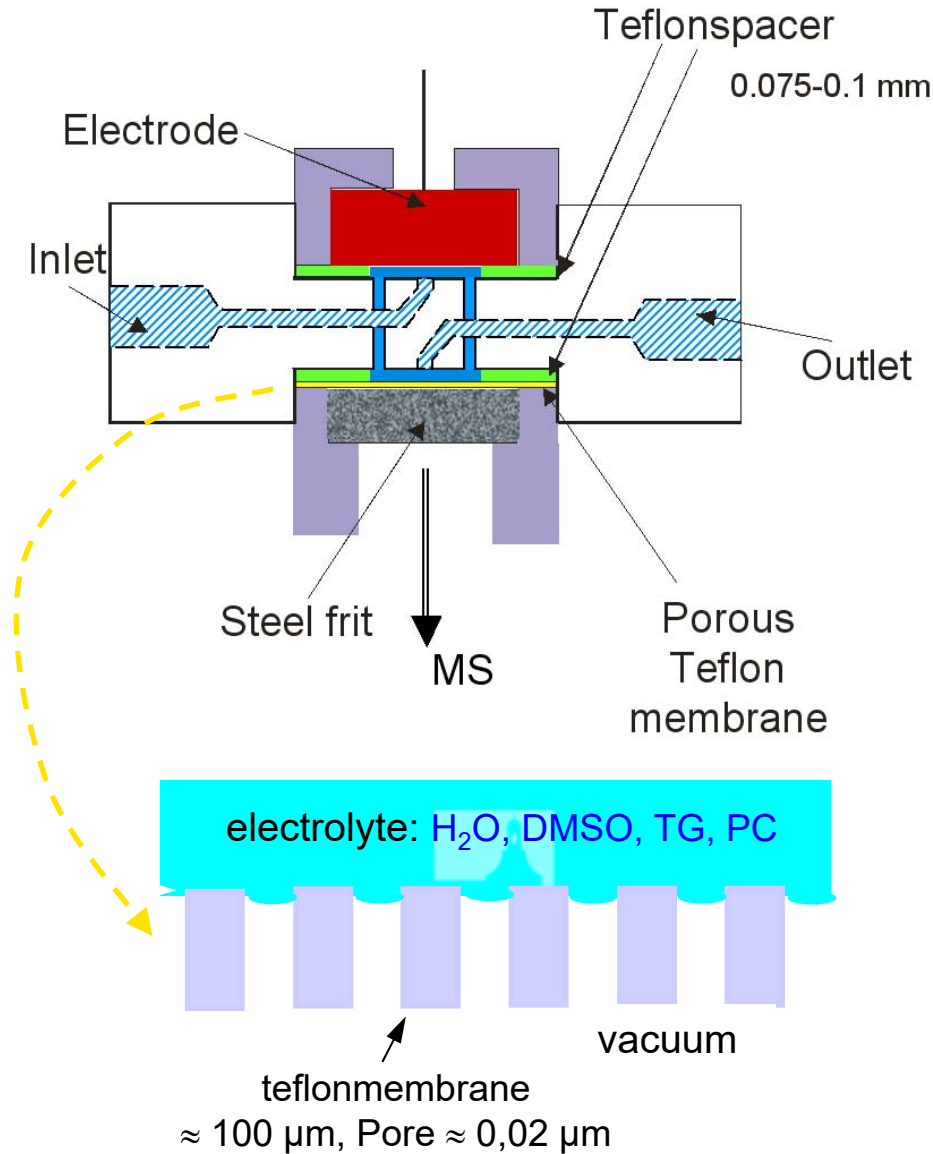
# Cathodic desorption of ads. ethene



E / mV vs. RHE  
 0,1 M H<sub>2</sub>SO<sub>4</sub>, v=10 mV/s, E<sub>ads</sub> =400mV;  
 CV dotted line: prior to adsorption



electrolyte flow (typ. 5  $\mu$ L/s)

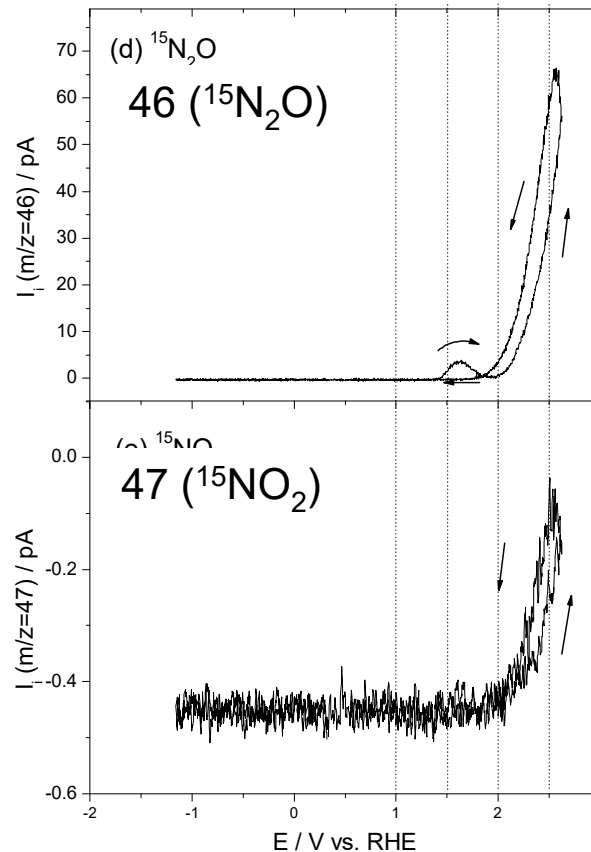
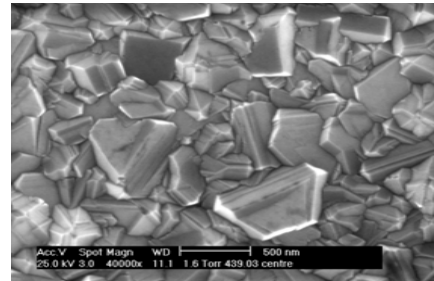
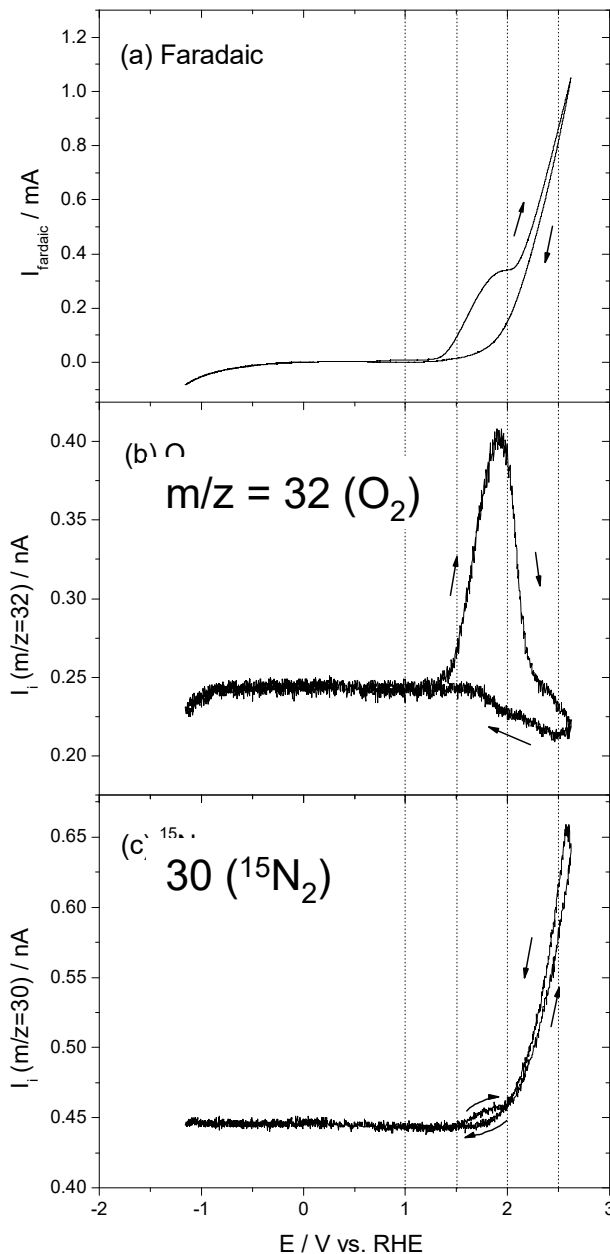


*n*  
*r*

- Best suited for continuous reactions
- Also suited for desorption reactions
- Defined convection and diffusion
- Detection limit: 0.1 ML  $\approx$  0,1 nmol

# example

# reactions at boron doped diamond (BDD)



oxidation of  $^{15}\text{NH}_4\text{OH}$   
 150mM at pH 12;  
 scan rate  $10 \text{ mV s}^{-1}$   
 flow rate  $5 \mu\text{l s}^{-1}$   
 1M  $\text{NaClO}_4$ ,

$$K^*(\text{O}_2) = \frac{4I_i(\text{O}_2)}{I_f}$$

$$I_f^*(\text{O}_2) = \frac{4I_i(\text{O}_2)}{K^*(\text{O}_2)}$$

$$CE(\text{O}_2) = \frac{I_f^*(\text{O}_2)}{I_f}$$

$$I_f^*(\text{species}) = \frac{ZI_{i,\text{species}}}{K^*(\text{O}_2)S}$$

S: sensitivity factor  
 - different ionization (and fragmentation) probabilities  
 $S=1, 1.65, \text{ and } 1.72$   
 for  $\text{N}_2, \text{N}_2\text{O}, \text{ and } \text{NO}_2$

However:  $K^*, N$  are  
 dependent on flow rate!

## flow through dual thin layer cell



limiting cases:

channel-electrode (diff. limitation)

$$I_F = 1.47 \cdot z \cdot F \cdot c \cdot D^{2/3} \cdot (A/b)^{2/3} \cdot u^{1/3}$$

wall-jet-electrode (diff. limitation)

$$I_F = 0.898 z \cdot F \cdot c \cdot D^{2/3} \cdot v^{-5/12} \cdot a^{-1/2} \cdot A^{3/8} \cdot u^{3/4}$$

very low flow rates

$$I_F = z \cdot F \cdot c \cdot u^1 \quad (\text{collection efficiency } f = 1)$$

$$I_F = zF \cdot a \cdot c \cdot u^y = g \cdot zF \cdot c \cdot D^{2/3} \cdot u^y \quad \text{with } y=1/3$$

$$I_i = K^0 \cdot a \cdot c \cdot u^x = g \cdot K^0 \cdot c \cdot D^{2/3} \cdot u^x \quad \text{with } x=1/3$$

diffusion limitation:

$$\text{channel electrode: } x = 1/3$$

$$(\text{wall jet: } x = 3/4)$$

$$\text{slow evaporation: } x = 0$$

$$u \rightarrow 0: x = 1$$

Rotating disc electrode:

$$i_{\text{lim}} = zF \frac{1}{1,61} \cdot D^{2/3} \cdot v^{-1/6} \cdot \omega^{1/2}$$

$$\delta_N = 1,61 D^{1/3} v^{1/6} \omega^{-1/2}$$

time constant:  $\tau = V/u = 5 \mu\text{L} / (5 \mu\text{L s}^{-1})$

independent of volatility

test for diffusion limitation

Merdon, C.; Fuhrmann, J. et al.: *Electrochimica Acta* **2016**, 211, 1

# flow through dual thin layer cell



general:

incoming flow  $J_i = dn/dt = \dot{n}$

ion current  $I_i = K^0 J_i$

electrochem. formation:  $J_i$  given by the far. current  $I_F$  :

$$J_i = N I_F / (z F)$$

$N$  : the transfer efficiency

$I_i = (K^*/z) I_F$ , with  $K^* = K^0 N / F$

calibration with known electrochem. reaction

$I_F = f_1 \cdot (z F \cdot c_{ed} \cdot u)$  collection efficiency:  $f(u) = \dot{n}_{react} / \dot{n}_{incom}$

$I_i = f_2 \cdot (K^0 \cdot c_p \cdot u)$   $u = dV/dt$

$c_p = I_F / (z F \cdot u)$

$I_i = f_2 K^0 I_F / (z F) = N K^0 I_F / (z F)$  **if complete mixing!**

The transfer efficiency  $N$  is then identical to the collection efficiency of the „detection“ cell  $f_2$  and independent of the electrochemical rate.

In general:  $N \neq f_2$

limiting cases:

channel-electrode (diff. limitation)

$$I_F = 1.47 \cdot z \cdot F \cdot c \cdot D^{2/3} \cdot (A/b)^{2/3} \cdot u^{1/3}$$

wall-jet-electrode (diff. limitation)

$$I_F = 0.898 z \cdot F \cdot c \cdot D^{2/3} \cdot v^{-5/12} \cdot a^{-1/2} \cdot A^{3/8} \cdot u^{3/4}$$

very low flow rates

$I_F = z \cdot F \cdot c \cdot u^1$  (collection efficiency  $f = 1$ )

$I_F = zF \cdot a \cdot c \cdot u^y = g \cdot zF \cdot c \cdot D^{2/3} \cdot u^y$  with  $y=1/3$

$I_i = K^0 \cdot a \cdot c \cdot u^x = g \cdot K^0 \cdot c \cdot D^{2/3} \cdot u^x$  with  $x=1/3$

diffusion limitation:

channel electrode:  $x = 1/3$

(wall jet:  $x = 3/4$ )

slow evaporation:  $x = 0$

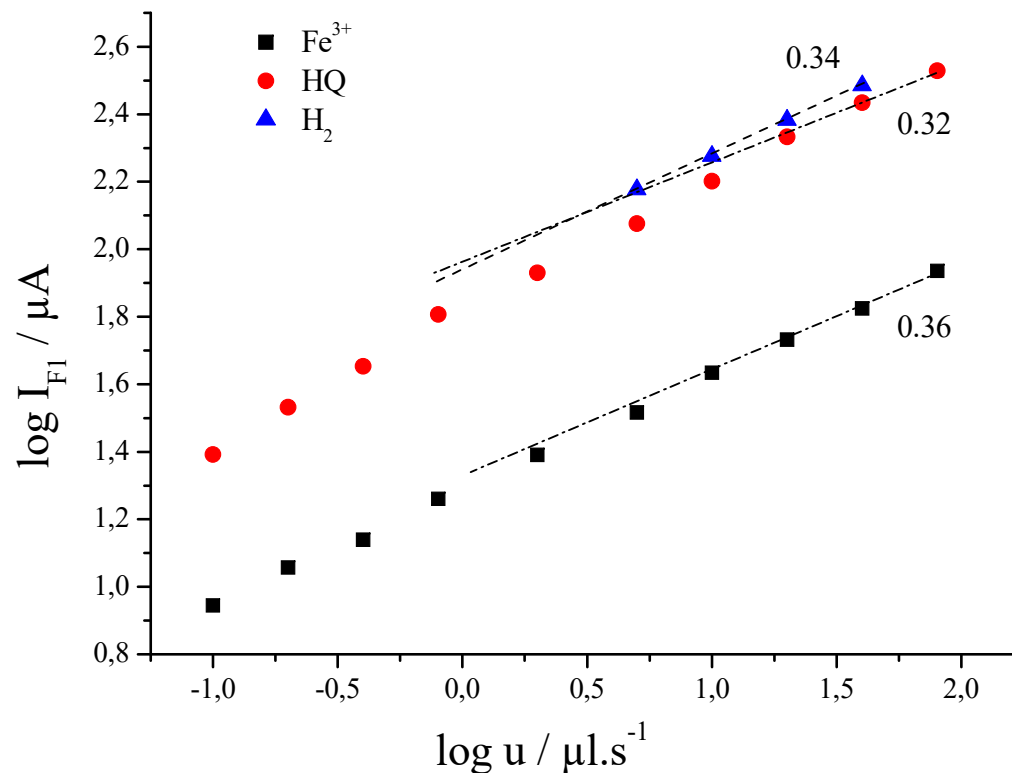
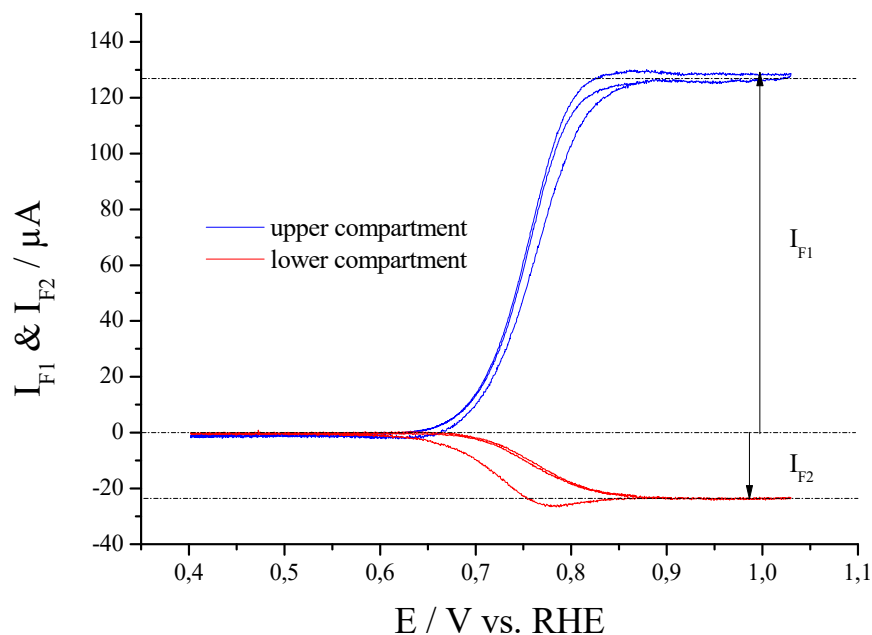
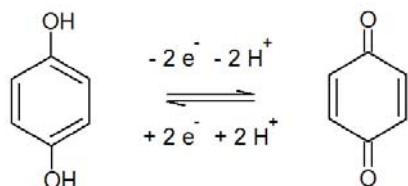
$u \rightarrow 0$ :  $x = 1$

time constant:  $\tau = V/u = 5 \mu L / (5 \mu L s^{-1})$

independent of volatility

test for diffusion limitation

# characterization: flow through dual thin layer cell



$10^{-3}$  M HQ in 0.5 M  $\text{H}_2\text{SO}_4$ ; 5 mV/s;  
 $E_1 = 0.4 - 1.1$  V,  
 detector electrode  $E_2 = 0.5$  V (const.);  
 electrolyte flow rate:  $5 \mu\text{l}\cdot\text{s}^{-1}$

Logarithmic diagrams of limiting current vs. flow rate  
 $10^{-3}$  M hydroquinone in 0.5 M  $\text{H}_2\text{SO}_4$ ,  
 $10^{-3}$  M  $\text{Fe}_2(\text{SO}_4)_3$  in 0.5 M  $\text{H}_2\text{SO}_4$   
 $\text{H}_2$  saturated 0.5 M  $\text{H}_2\text{SO}_4$   
 5 mV/s

# solubility and diff. coeff. of volatile species from flow rate dependence



low flow rates:

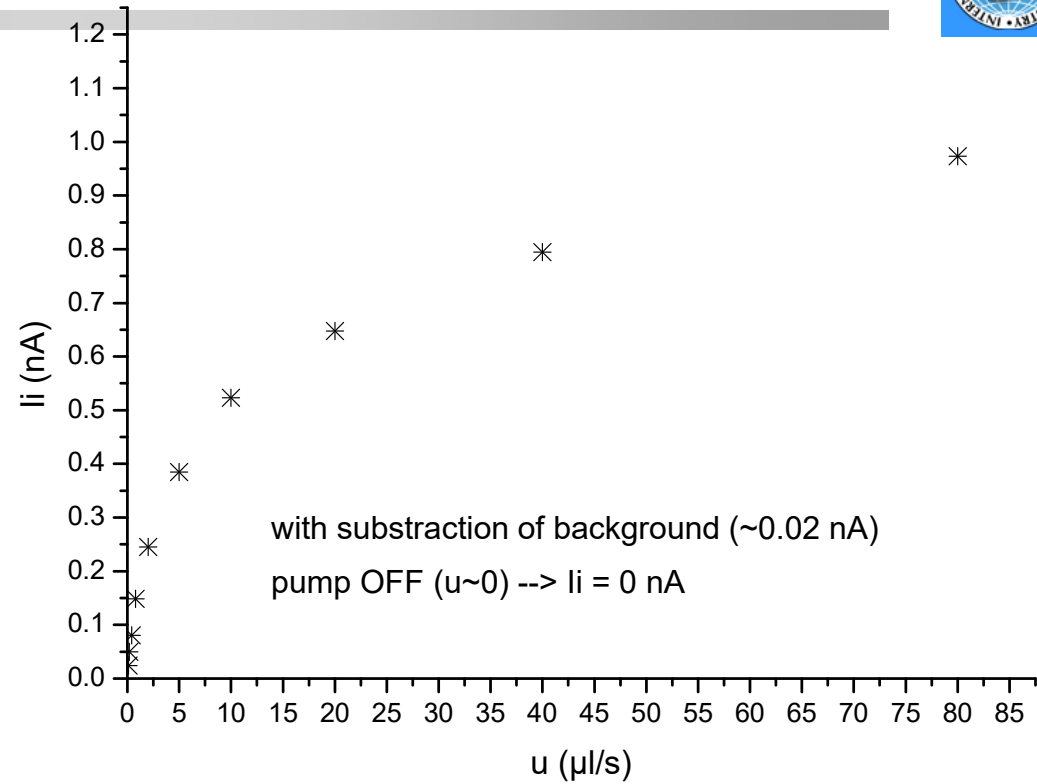
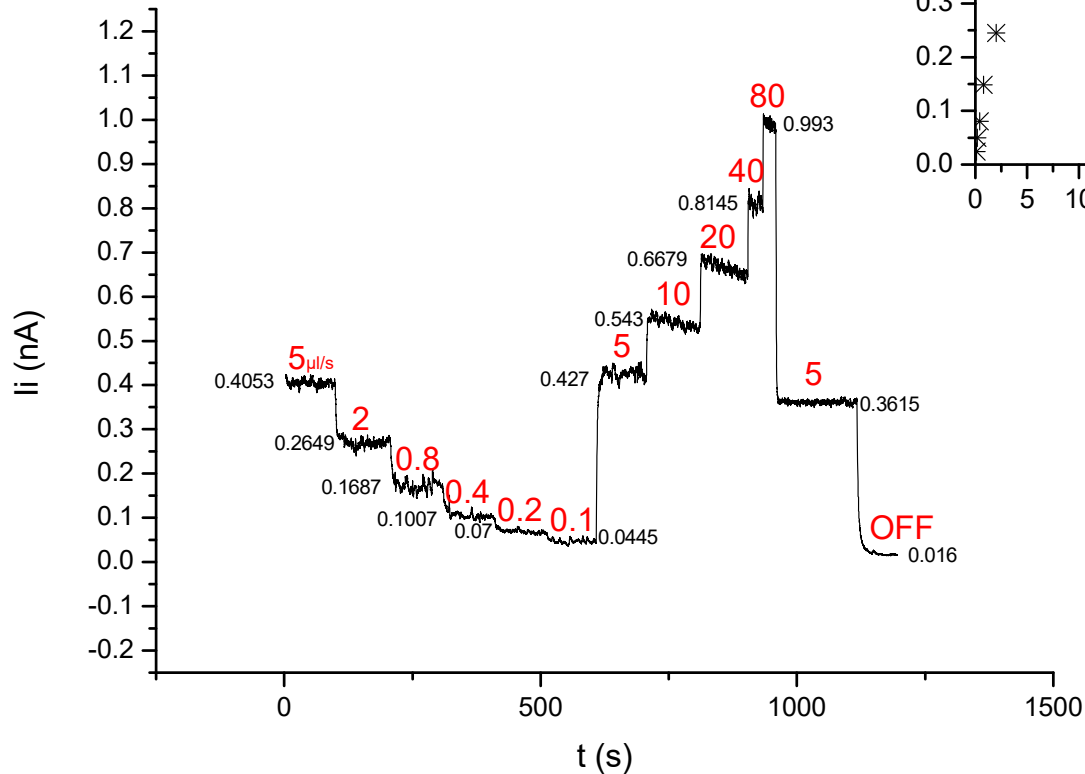
$$I_i = K^0 \cdot a \cdot c \cdot u^x \quad \text{with } x=1$$

==> c

high flow rates:

$$I_i = g \cdot K^0 \cdot c \cdot D^{2/3} \cdot u^x \quad \text{with } x=1/3$$

==> D



with subtraction of background (~0.02 nA)

pump OFF (u~0) --> li = 0 nA

O<sub>2</sub> saturated Propylene Carbonate

m/z=32

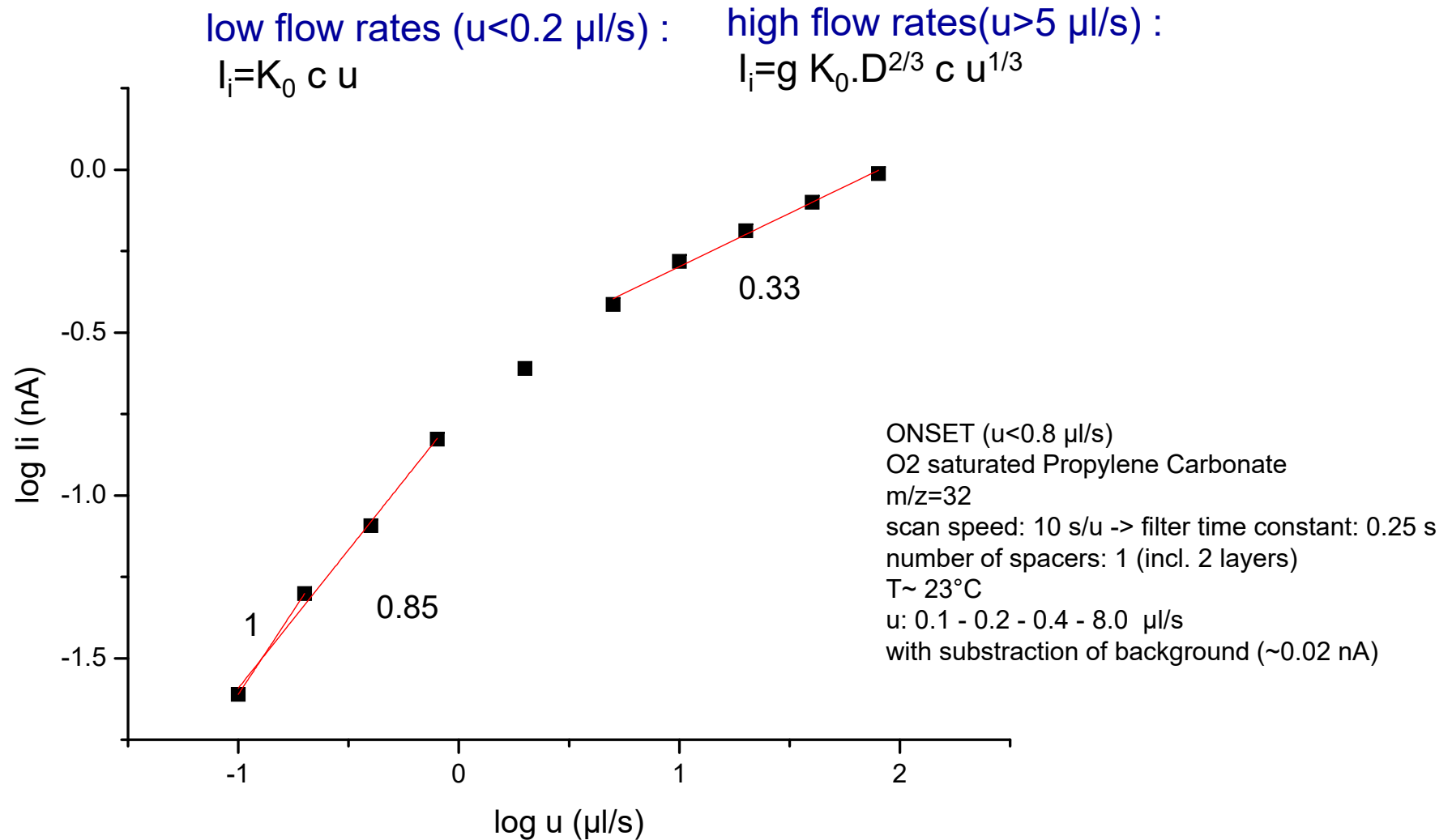
scan speed: 10 s/u -> filter time constant: 0.25 s

number of spacers: 1 (incl. 2 layers)

T~ 23°C

u: 0.1 - 0.2 - 0.4 - 8.0 - 2 - 5 - 10 - 20 - 40 - 80 µl/s

# Conc. and diff. coeff. from flow rate dependence





# Conc. and diff. coeff. from flow rate dependence



low flow rates ( $u < 0.2 \mu\text{l/s}$ ) :

$$I_i = K_0 c u$$

$$I_i/u = K_0 c = 0.255 \text{ nA}/\mu\text{l}\cdot\text{s}^{-1}$$

$$\rightarrow c = 0.255 / K_0$$

$$\text{with } K_0 = 0.062 \text{ nA}/\text{nmol}\cdot\text{s}^{-1}$$

$\rightarrow$

$$c = 4.08 \text{ mM (Lit: 4.8 mM)}$$

high flow rates ( $u > 5 \mu\text{l/s}$ ) :

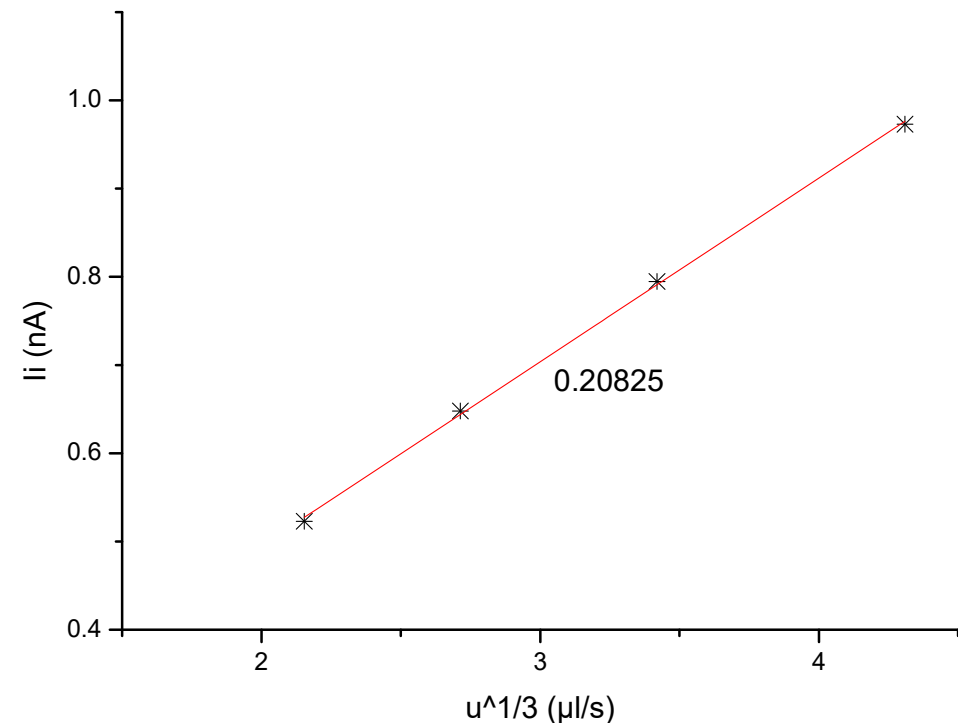
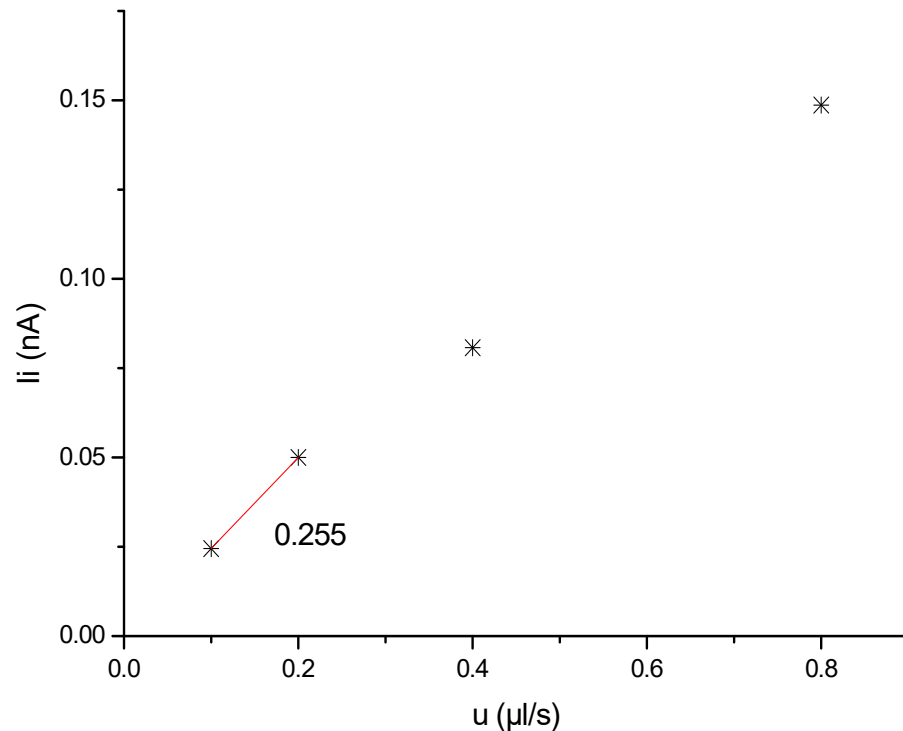
$$I_i = G K_0 D^{2/3} c u^{1/3}$$

$$\text{with } G (\text{Geometry Factor}) = 12.4 \text{ cm}^{2/3}$$

$$c (\text{Oxygen Solubility}) = 4.08 \text{ mM}$$

$\rightarrow$

$$D = 18 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1} (\text{Lit: } 25 \cdot 10^{-6})$$

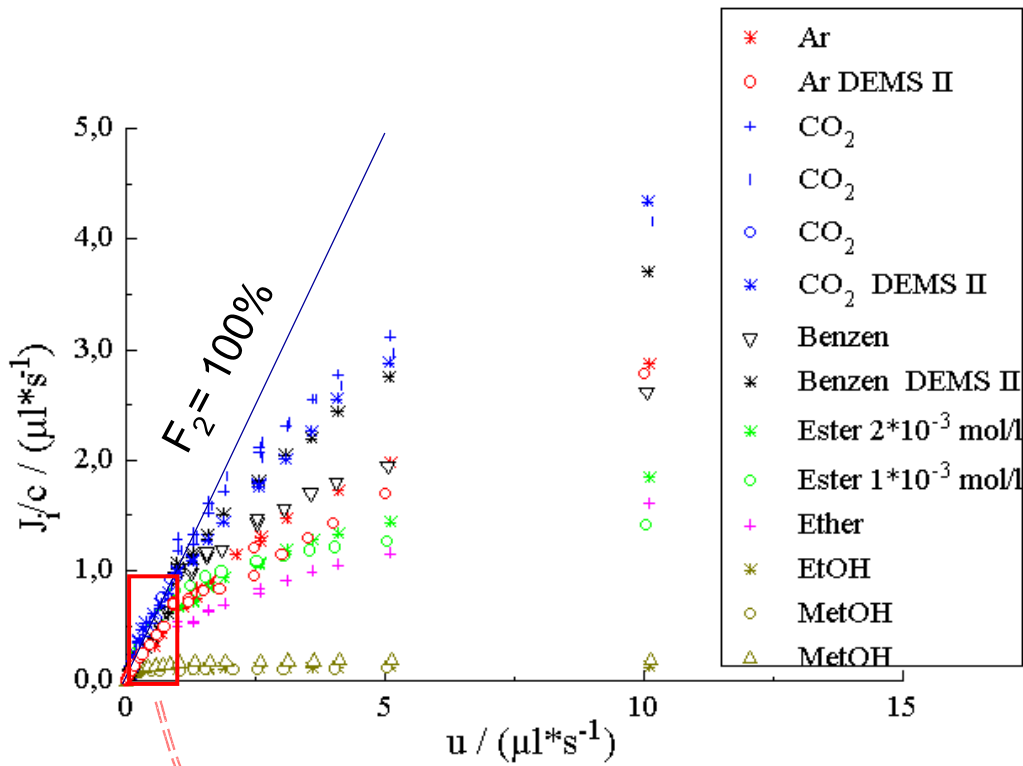


## O<sub>2</sub> solubilities and diffusion coefficients



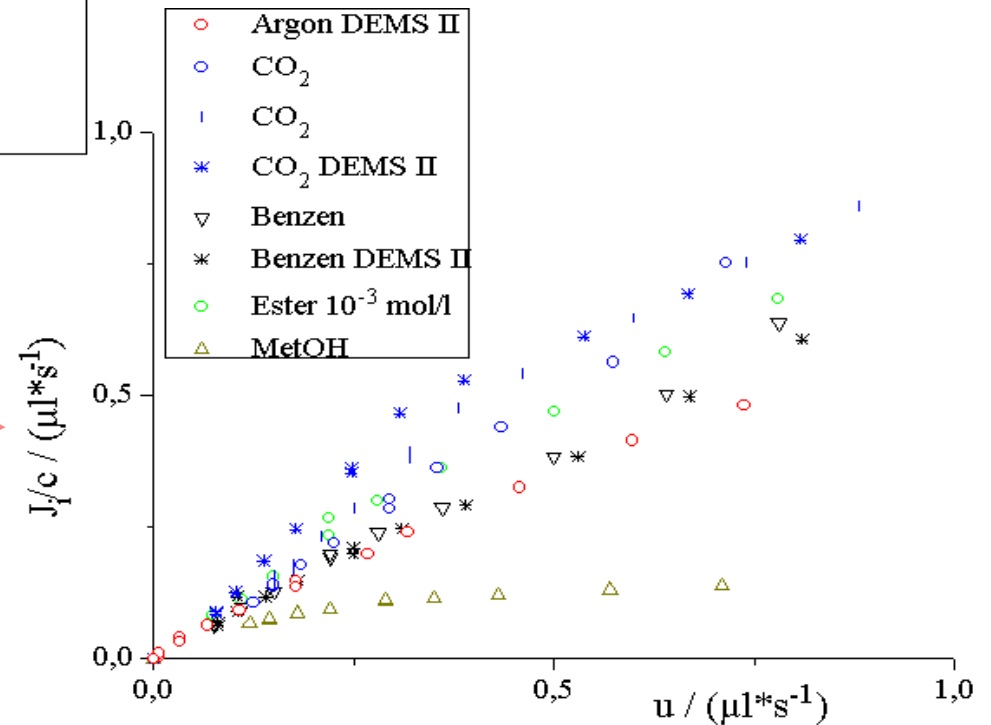
solvent	C (mM)	Lit	D <sub>x=1/3</sub> /(*10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup> )	Lit
0.1 M LiOH	0.785	0.8	20.1	19
1 M LiOH	0.5	0.6	20	18.6
0.1 M KOH	1.33	1.2	24.4	20
1 M KOH	0.867	0.9	20.6	18
2.5 M KOH	0.478	0.4	17.78	15
PC	3.53	3.6	19.4	25+- 8
PC+0.1 M LiClO <sub>4</sub>	2.9	n.f.	16.2	n.f.
PC+1 M LiClO <sub>4</sub>	1.95	n.f.	9.6	n.f.
DMSO	2.07	2.1	15.04	16
DMSO+0.1 M Mg(ClO <sub>4</sub> ) <sub>2</sub>	1.11	n.f.	14.05	n.f.
DMSO+0.5 M Mg(ClO <sub>4</sub> ) <sub>2</sub>	0.763	n.f.	10.6	n.f.
DMSO+0.1 M LiClO <sub>4</sub>	3.2	n.f.	17.97	n.f.
DMSO+1 M LiClO <sub>4</sub>	2.4	n.f.	13.77	n.f.

# The mass spectrometric compartment: different solutes



diffusion limitation  
for gases and volatile,  
less soluble species

For less volatile species:  
 $J_i \rightarrow \text{const}\cdot u^0$



## flow through dual thin layer cell



limiting cases:

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$$I_F = 1.47 \cdot z \cdot F \cdot c \cdot D^{2/3} \cdot (A/b)^{2/3} \cdot u^{1/3}$$

wall-jet-electrode (diff. limitation)

$$I_F = 0.898 z \cdot F \cdot c \cdot D^{2/3} \cdot v^{-5/12} \cdot a^{-1/2} \cdot A^{3/8} \cdot u^{3/4}$$

very low flow rates

$$I_F = z \cdot F \cdot c \cdot u^1 \quad (\text{collection efficiency } f = 1)$$

$$I_F = zF \cdot a \cdot c \cdot u^y = g \cdot zF \cdot c \cdot D^{2/3} \cdot u^y \quad \text{with } y=1/3$$

$$I_i = K^0 \cdot a \cdot c \cdot u^x = g \cdot K^0 \cdot c \cdot D^{2/3} \cdot u^x \quad \text{with } x=1/3$$

diffusion limitation:

channel electrode:  $x = 1/3$

(wall jet:  $x = 3/4$ )

slow evaporation:  $x = 0$

$u \rightarrow 0$ :  $x = 1$

test for diffusion limitation

Limitation by evaporation (Henry's law):

$$\begin{aligned} J_i &= A \cdot k_p \cdot p_i^{surf} \\ &= A \cdot k_p \cdot K_H \cdot c = S \cdot p_i / RT \\ \Rightarrow p_i &= RT A \cdot k_p \cdot K_H \cdot c / S \\ I_i &= a \cdot p_i = a \cdot RT A \cdot \frac{1}{S} \cdot k_p \cdot K_H \cdot c \end{aligned}$$

Rotating disc electrode:

$$i_{lim} = zF \frac{1}{1,61} \cdot D^{2/3} \cdot v^{-1/6} \cdot \omega^{1/2}$$

$$\delta_N = 1,61 D^{1/3} v^{1/6} \omega^{-1/2}$$

Substanz	x für u < 0.8 µl/s	x für u > 0.8 µl/s
Argon		0.61
Argon DEMS II	0.94	0.65
CO <sub>2</sub>		0.58
CO <sub>2</sub>	1	
CO <sub>2</sub>	1.05 bis 0.83	0.55
CO <sub>2</sub> DEMS II	0.96	0.66
Benzen	1	0.45
Benzen DEMS II	0.95	0.6
Ester (c=2·10 <sup>-3</sup> M)		0.48 bis 0.33
Ester (c=1·10 <sup>-3</sup> M)	1 bis 0.82	0.31
Ether		0.51
Ethanol		0.11
Methanol		0.12
Methanol	0.74 bis 0.41	0.09

$$I_F = z F \cdot a \cdot c \cdot u^y \quad u = dV/dt$$

$$I_i = K_0 \cdot a \cdot c_p \cdot u^x$$

diffusion limitation:

channel electrode: x = 1/3

wall jet: x = 3/4

slow evaporation: x = 0

u ----> 0: x = 1

diffusion limitation  
for gases and volatile,  
less soluble species

## flow through dual thin layer cell

general:

incoming flow  $J_i = dn/dt = \dot{n}$

ion current  $I_i = K^0 J_i$

electrochem. formation:  $J_i$  given by the far. current  $I_F$  :

$$J_i = N I_F / (z F)$$

$N$  : the transfer efficiency

$I_i = (K^*/z) I_F$ , with  $K^* = K^0 N / F$

calibration with known electrochem. reaction

$I_F = f_1 \cdot (z F \cdot c_{ed} \cdot u)$  collection efficiency:  $f(u) = \dot{n}_{react} / \dot{n}_{incom}$

$I_i = f_2 \cdot (K^0 \cdot c_p \cdot u)$   $u = dV/dt$

$c_p = I_F / (z F \cdot u)$

$I_i = f_2 K^0 I_F / (z F) = N K^0 I_F / (z F)$  **if complete mixing!**

The transfer efficiency  $N$  is then identical to the collection efficiency of the „detection“ cell  $f_2$  and independent of the electrochemical rate.

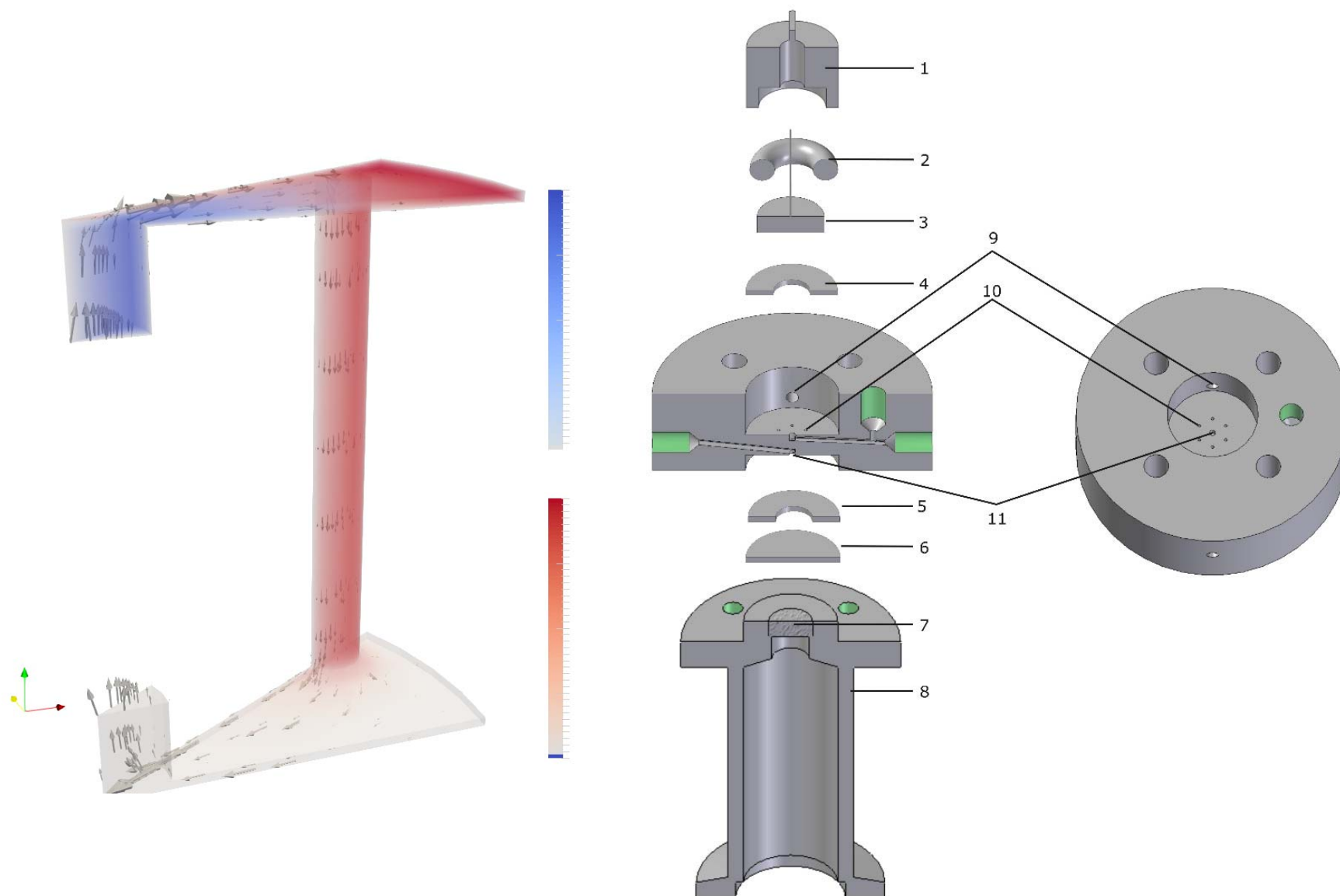
In general:  $N \neq f_2$

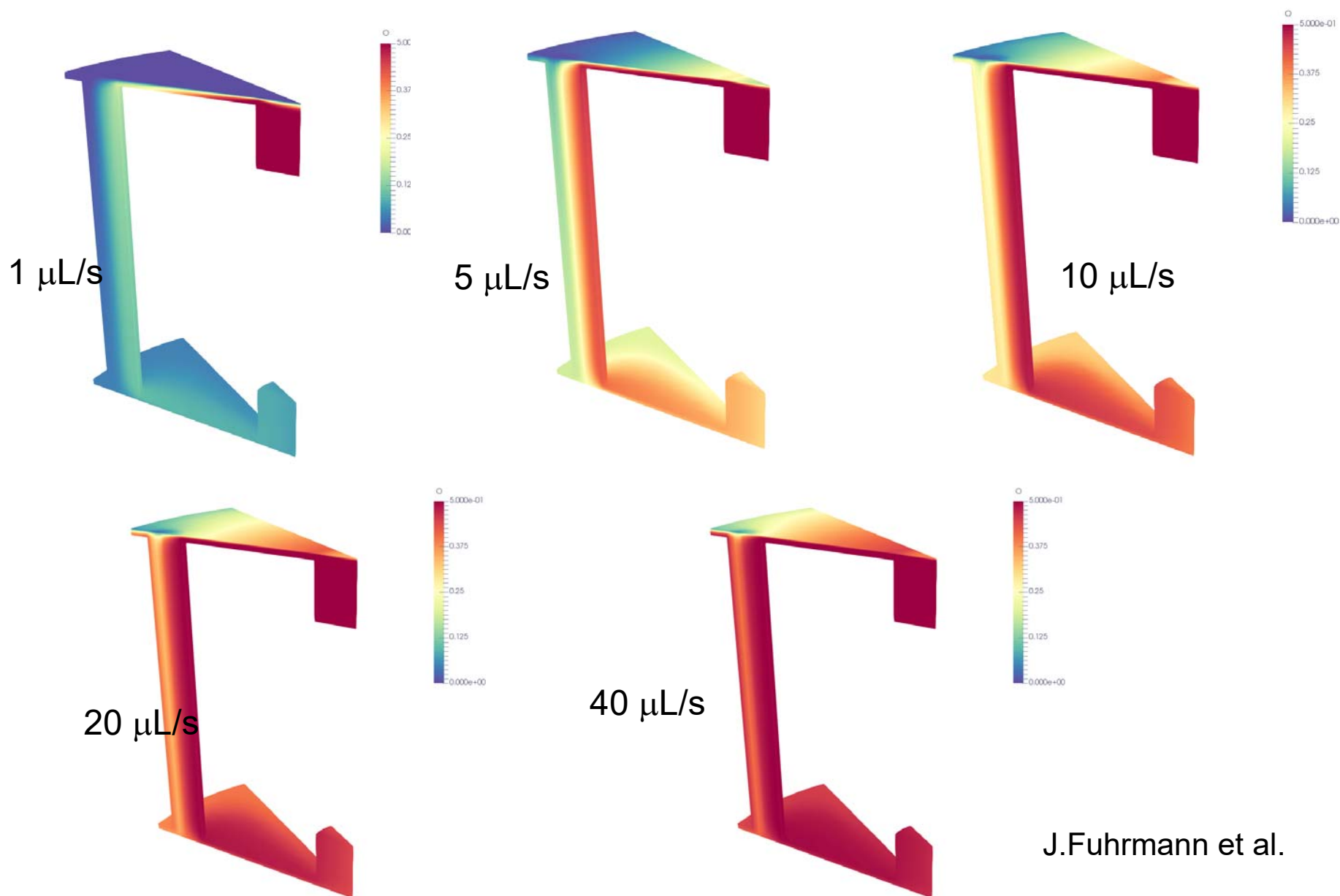
**If complete mixing:  
Calibration for  
 $(f_2 \cdot K^0) = N \cdot K^0$   
with solution  $c_p$**

time constant:

$$\tau = V/u = 5 \mu\text{L} / (5 \mu\text{L s}^{-1})$$

**independent of volatility**





J.Fuhrmann et al.



## Further examples and cell types

# Methanol oxidation: product formation rates



Measurement of

- Faradaic current
- rate of CO<sub>2</sub> formation
- rate of CH<sub>3</sub>OOCH formation
- CH<sub>3</sub>OH consumption

• reaction order:

- 0.4 for current,
- 0.14 for CO<sub>2</sub> formation

Influence of catalyst layer thickness  
(for 0.1 M CH<sub>3</sub>OH)

on current efficiency A for CO<sub>2</sub>:

Smooth Pt: A = 20 % (independent of flow rate)

XC 72:

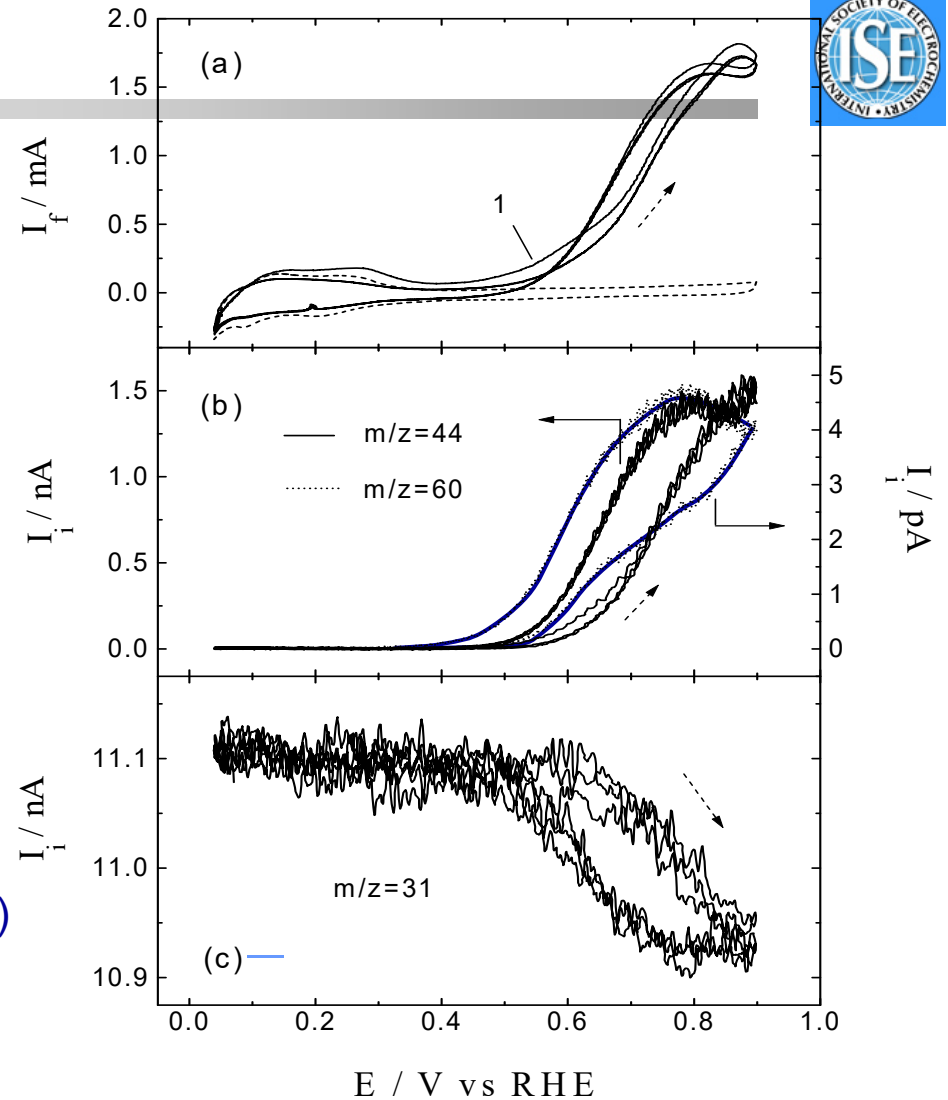
10 μg Pt cm<sup>-2</sup>: A = 30 - 50%

0.6 mg Pt cm<sup>-2</sup>: A ≈ 95%

$$A = \frac{n_{CO_2} \cdot 6F}{I_f}$$

⇒ Minimal catalyst layer thickness needed

⇒ Parallel path mechanism



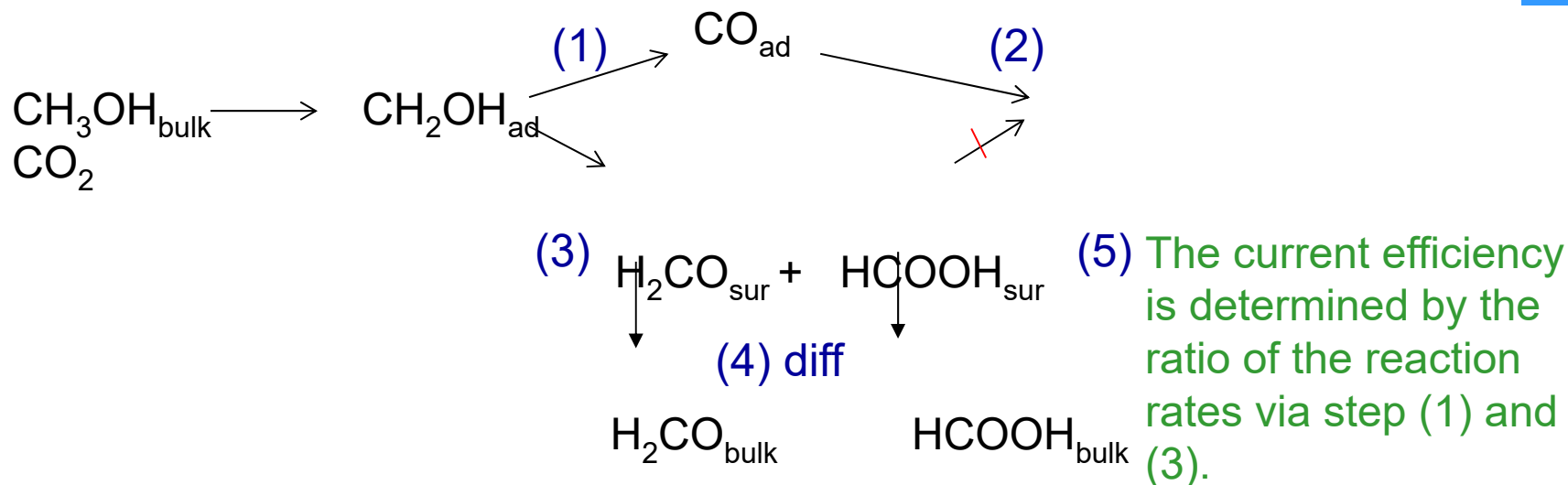
Ecf03.org

Wang et al., Fig.3

Methanol ox. on Vulcan XC-72 / 40% Pt  
(0.6 mg Pt cm<sup>-2</sup>) supported on GC in  
0.1M + CH<sub>3</sub>OH 0.5M H<sub>2</sub>SO<sub>4</sub>. 10mV s<sup>-1</sup>, 5μL

H. Wang, T. Löffler, H. Baltruschat, *J. Appl. Electrochem.* **2001**, 31, 759s-1.

H. Wang, C. Windgenger, H. Baltruschat, M. Lopez, M. T. Reetz, *J. Electroanal. Chem.* **2001**, 509, 163.



### Influence of catalyst layer thickness

(for 0.1 M CH<sub>3</sub>OH)

on current efficiency A for CO<sub>2</sub>:

Smooth Pt: A = 20 % (independent of flow rate)

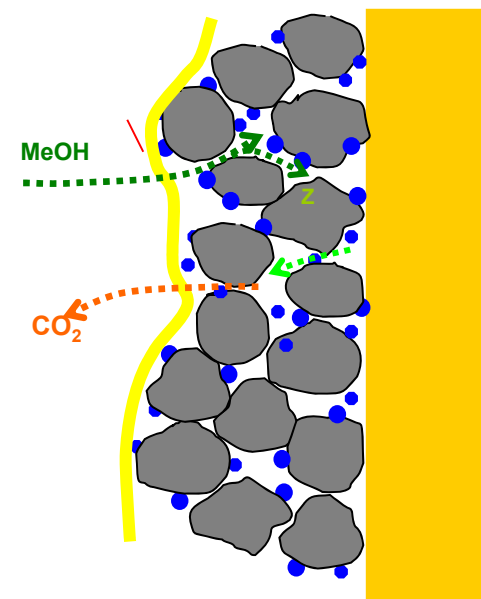
XC 72:

10 μg Pt cm<sup>-2</sup>: A = 30 - 50%

0.6 mg Pt cm<sup>-2</sup>: A ≈ 95%

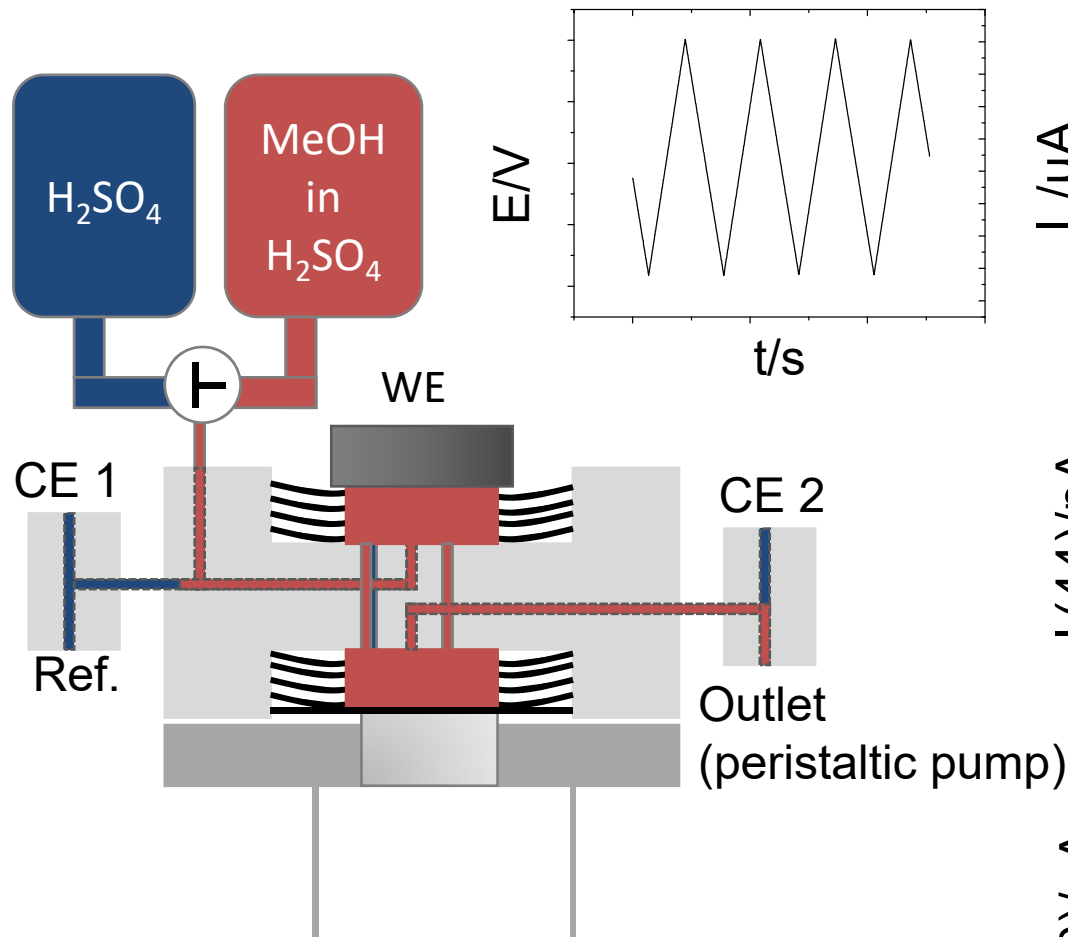
⇒ Minimal catalyst layer thickness needed

⇒ Parallel path mechanism



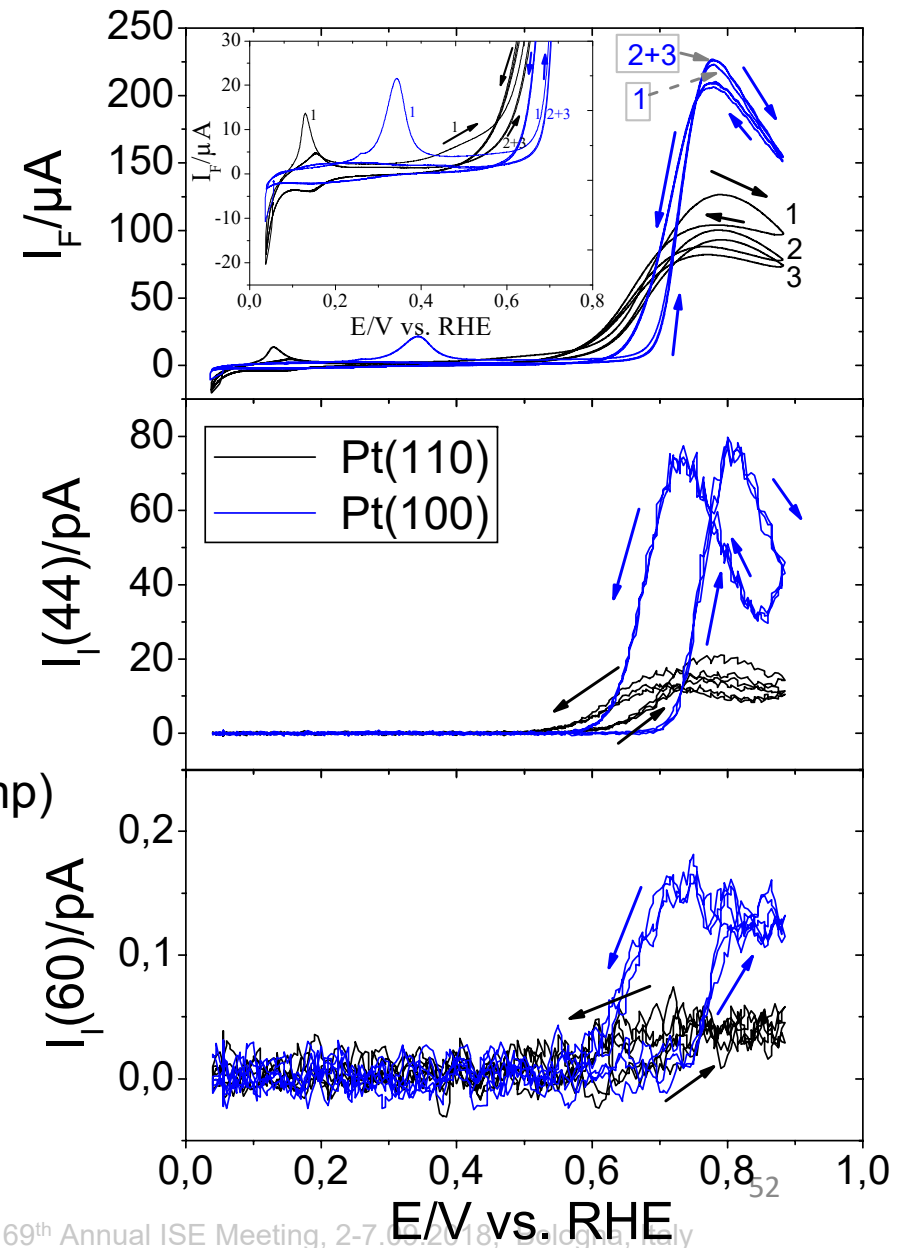
rates of single steps?

# Bulk-Oxidation of MeOH

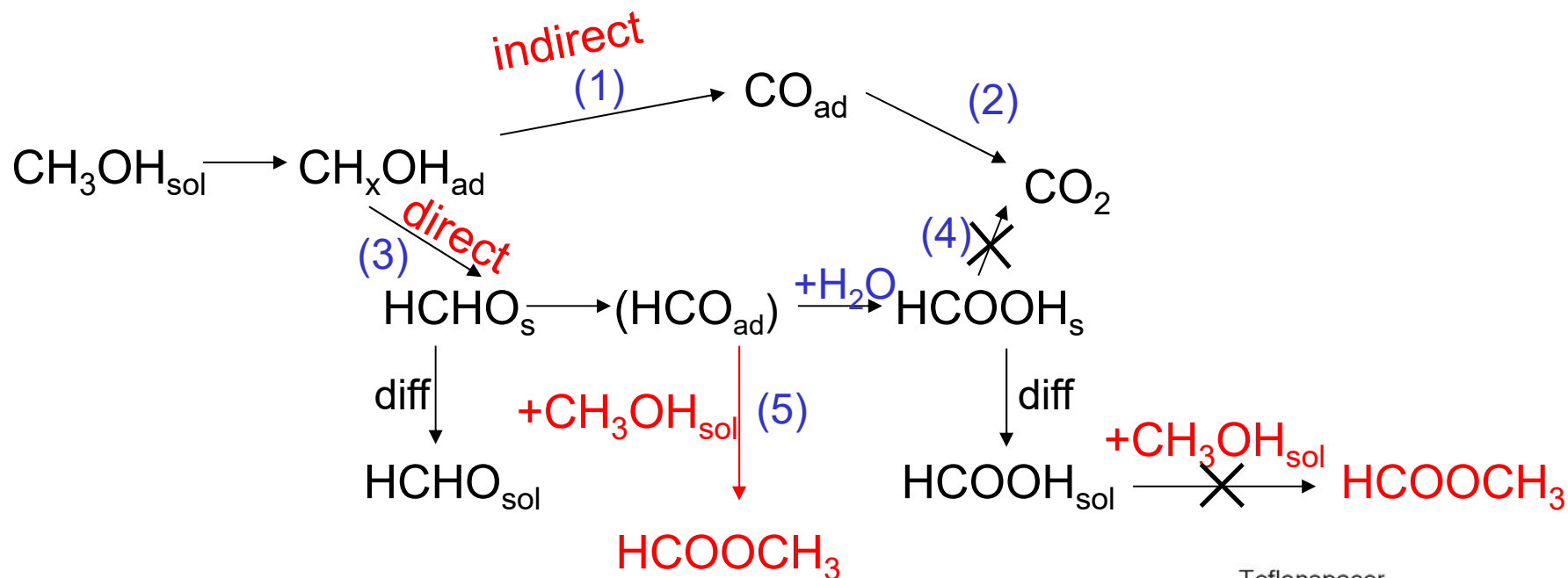


**MeOH:** 0,1 M MeOH +  
0,5 M  $\text{H}_2\text{SO}_4$  (supporting electrolyte)

18.05.2021



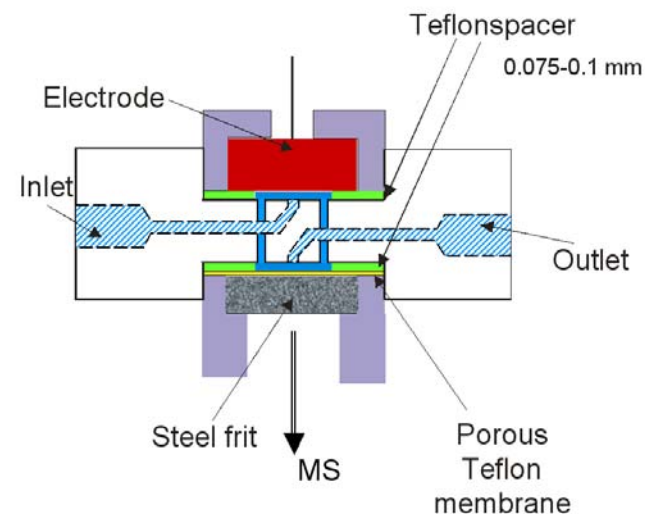
## Pathways of methanol oxidation



DEMS: formation rate of

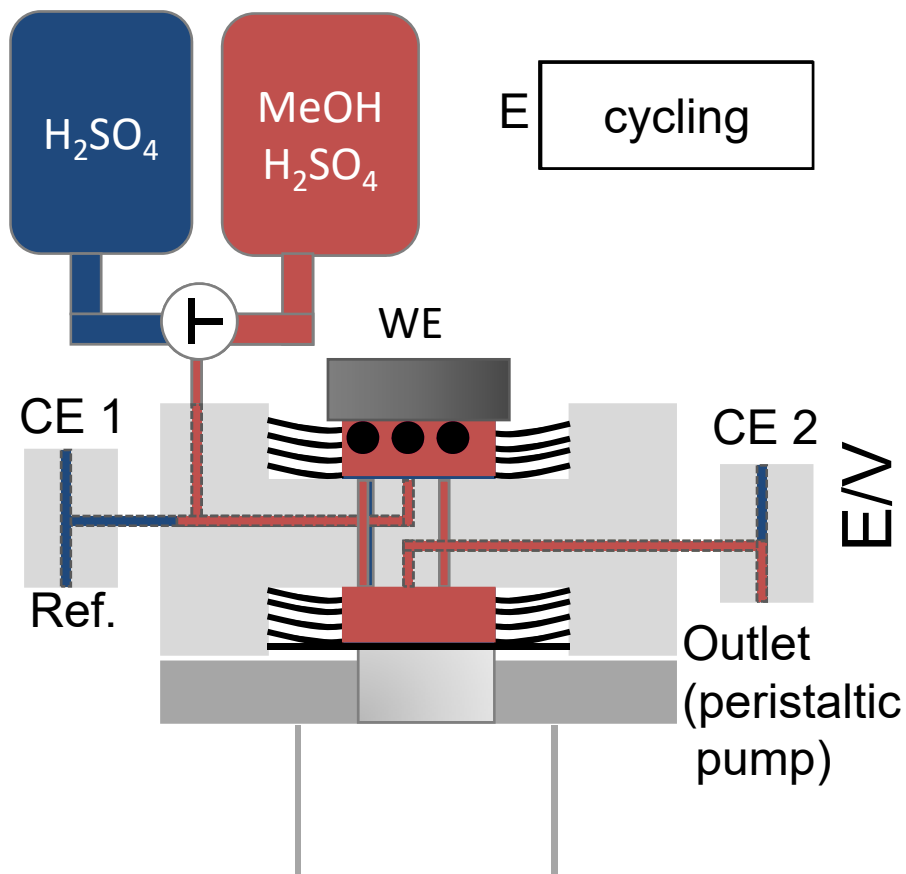
- CO<sub>2</sub>
- methylformate
- current efficiencies
- dependence on flow rate

important: rate of single reaction steps

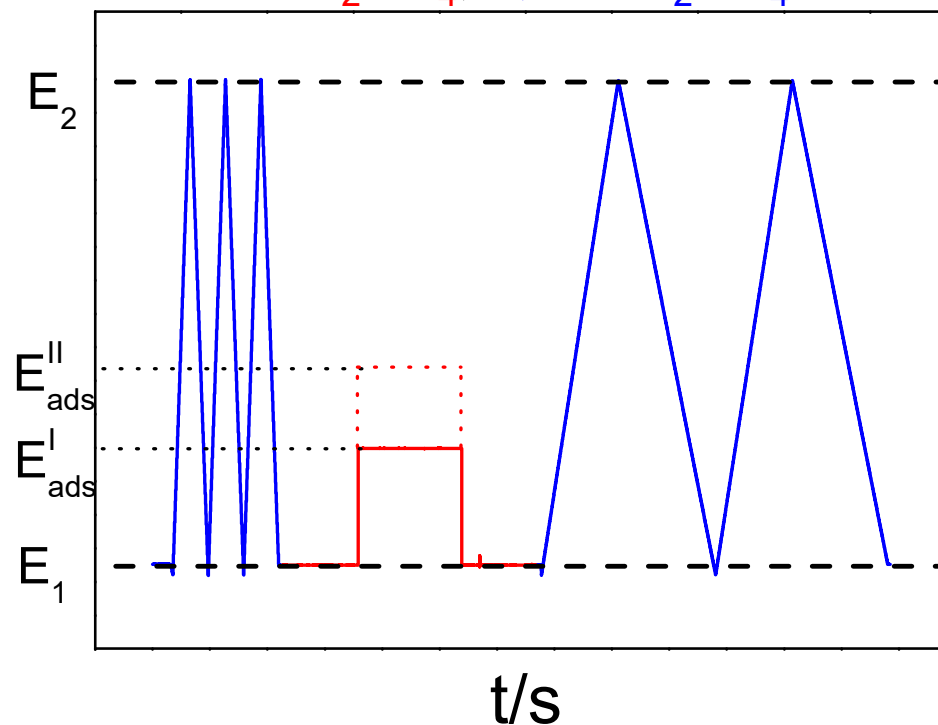


Wang, H.; Wingender, C.; Baltruschat, H.; Lopez, M.; Reetz, M. T., *J. Electroanal. Chem.* **2001**, 509, 163.  
 Abd-El-Latif, A. A.; Baltruschat, H., *J. Electroanal. Chem.* **2011**, 662, 204

# Electrolyte exchange: MeOH-ads. and oxidation of the adsorbate



Electrolyte exchange:  
 MeOH + H<sub>2</sub>SO<sub>4</sub>, 0,5 M H<sub>2</sub>SO<sub>4</sub>



no adsorption of adsorbates occurs at 0,05 V

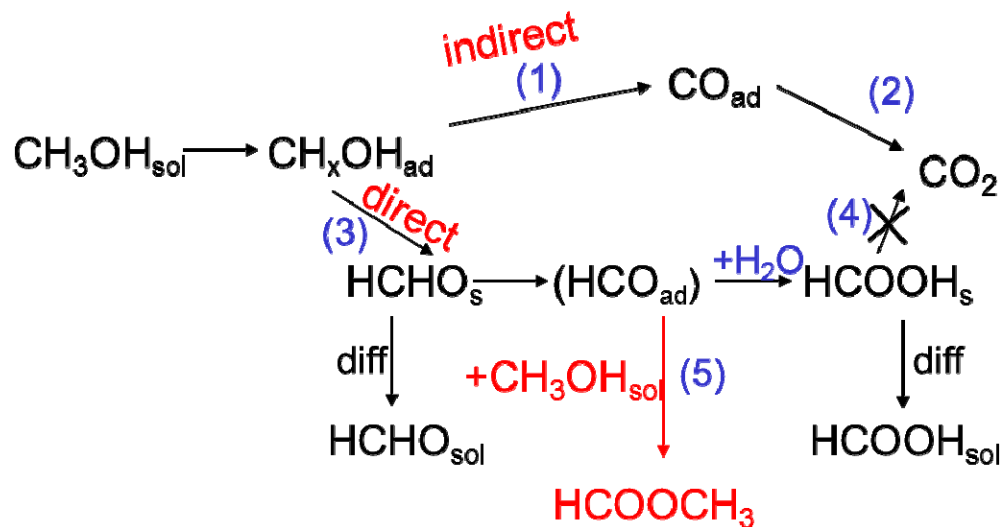
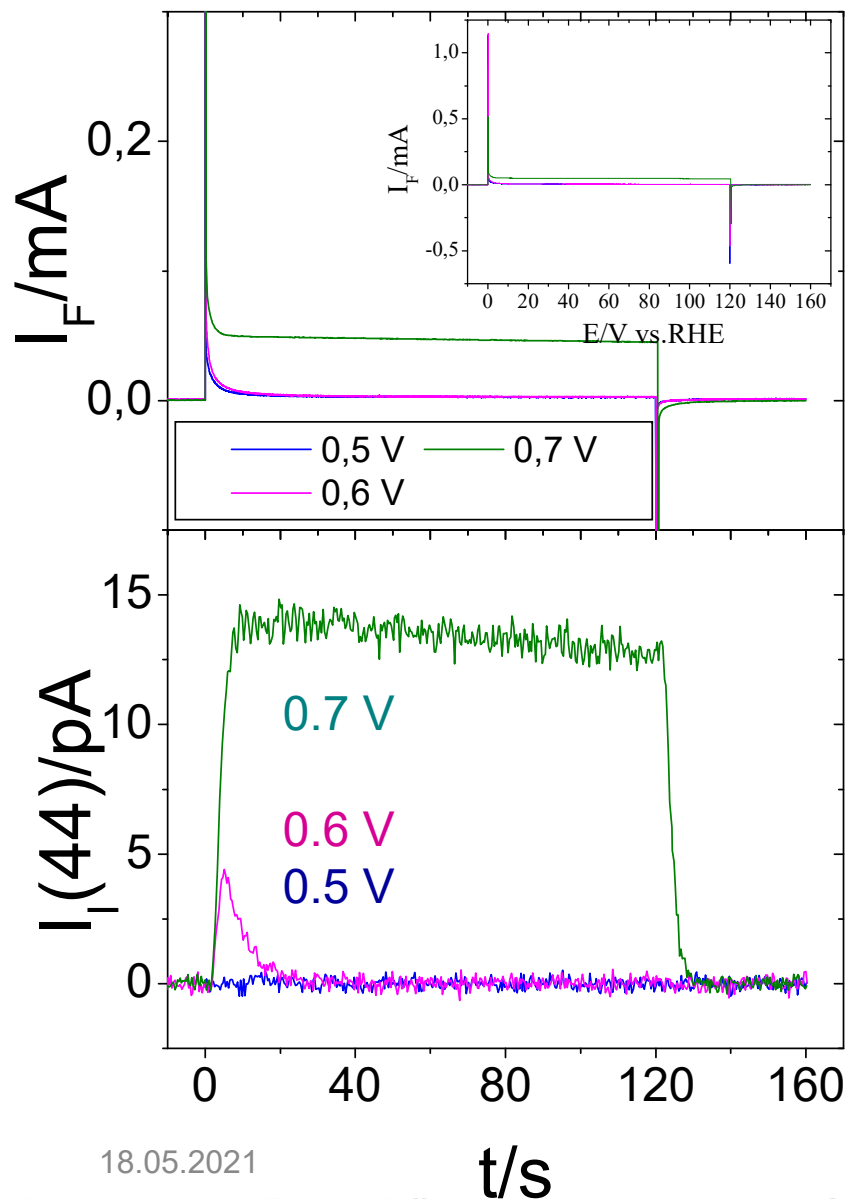
Series of experiments with different adsorption times and potentials are performed to investigate the adsorbate coverage.

18.05.2021

# methanol ox. at constant potential



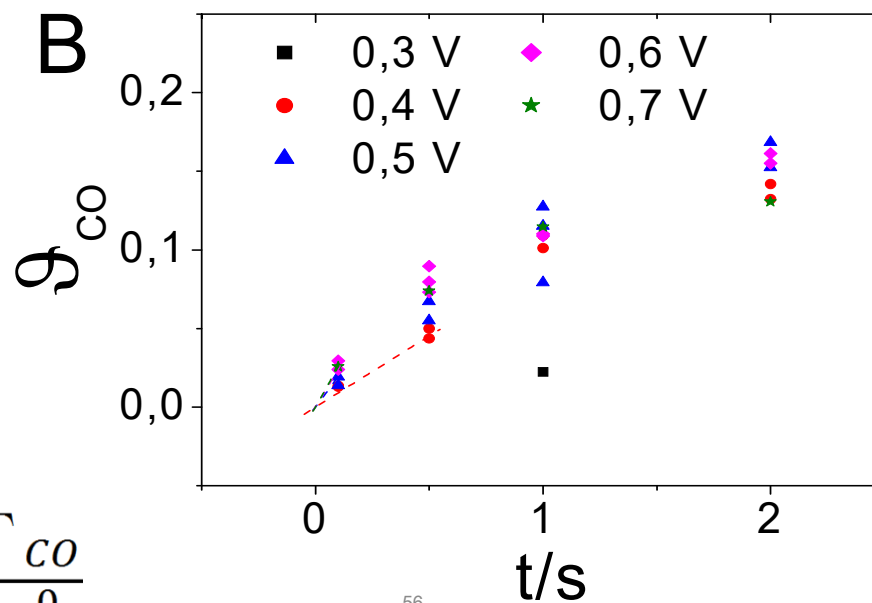
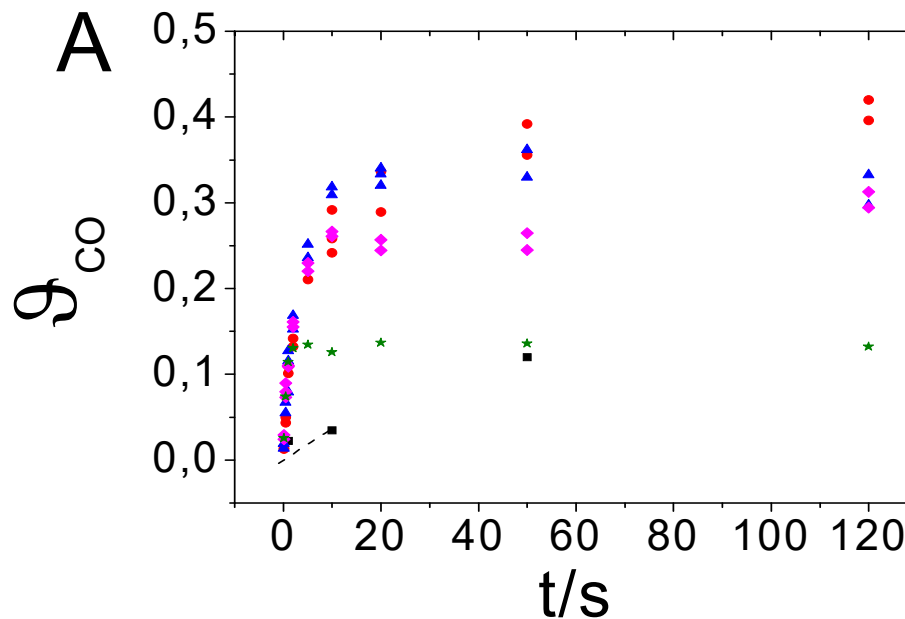
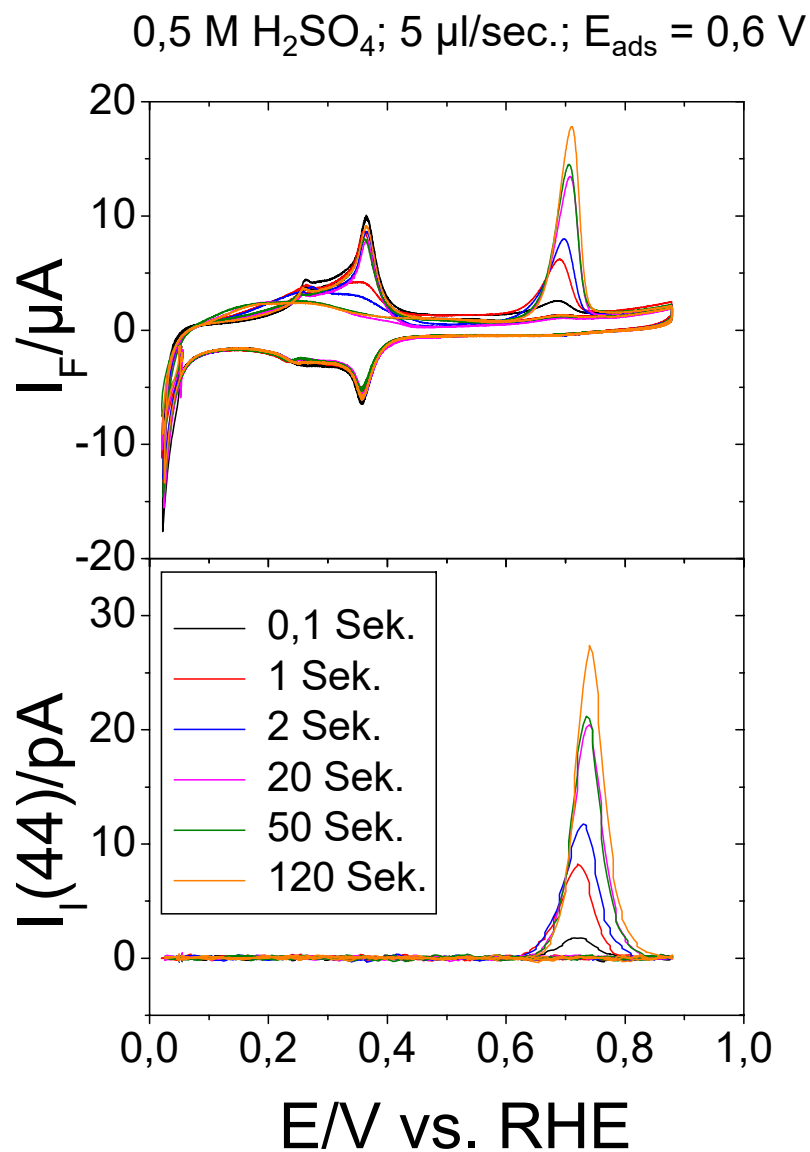
0,01 M MeOH + 0,5 M H<sub>2</sub>SO<sub>4</sub>; 5 μl/sec.



transient:  
fast (1) + (2), then blocking by CO<sub>ad</sub>

$$(2): v = k \theta (1 - \theta)$$

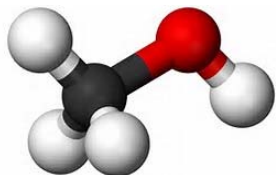
# MeOH adsorbate oxidation on Pt(100) and $\vartheta(t)$



$$\vartheta_{CO} = \frac{\Gamma_{CO}}{\Gamma_H^0}$$

18.05.2021

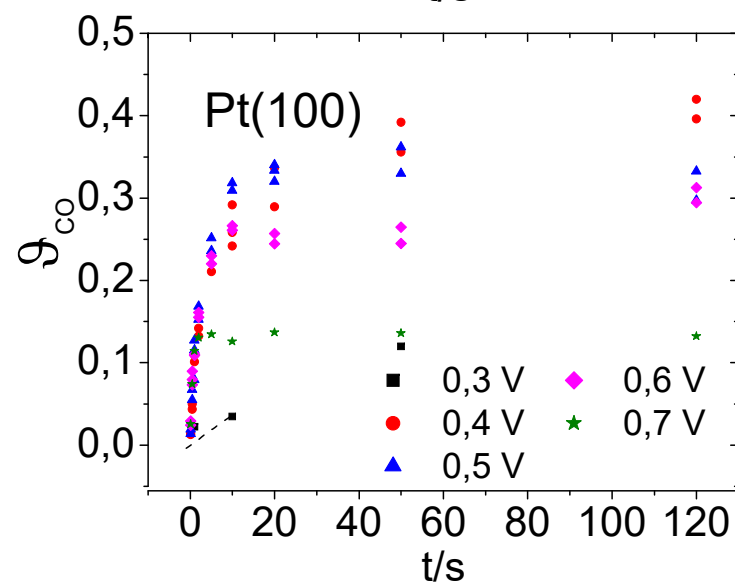
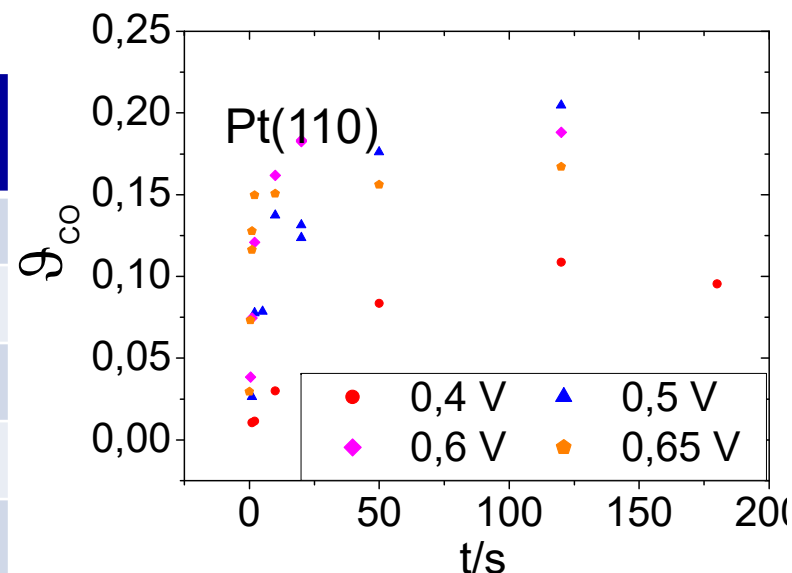




# Current efficiency for CO<sub>2</sub> and $\vartheta(t)$



Surface	MeOH-conc. /mol/l	rate / $\mu$ l/s	A44 %	A44%	A44 %
			c.e	c.e	c.e
			0,6 V	0,65 V	0,7 V
Pt(pc)	0,1	2	14	16	25
	0,1	5	13	17	25
	0,1	10	12	17	24
	0,01	5	23	n. d.	41
Pt(100)	0,1	5	n. d.	n. d.	63
	0,01	5	n. d.	n. d.	70
Pt(110)	0,01	2	13	33	n. d.
	0,01	5	12	32	n. d.
	0,01	10	13	n. d.	n. d.

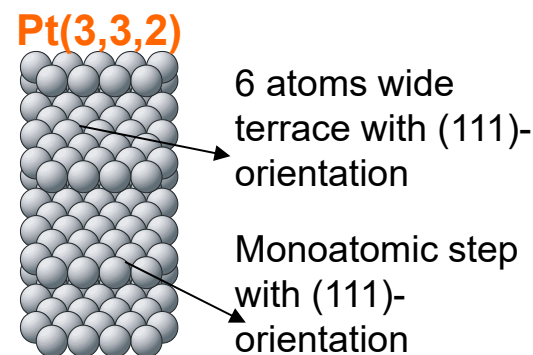
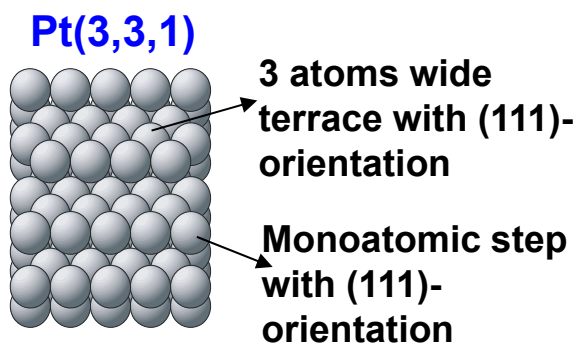
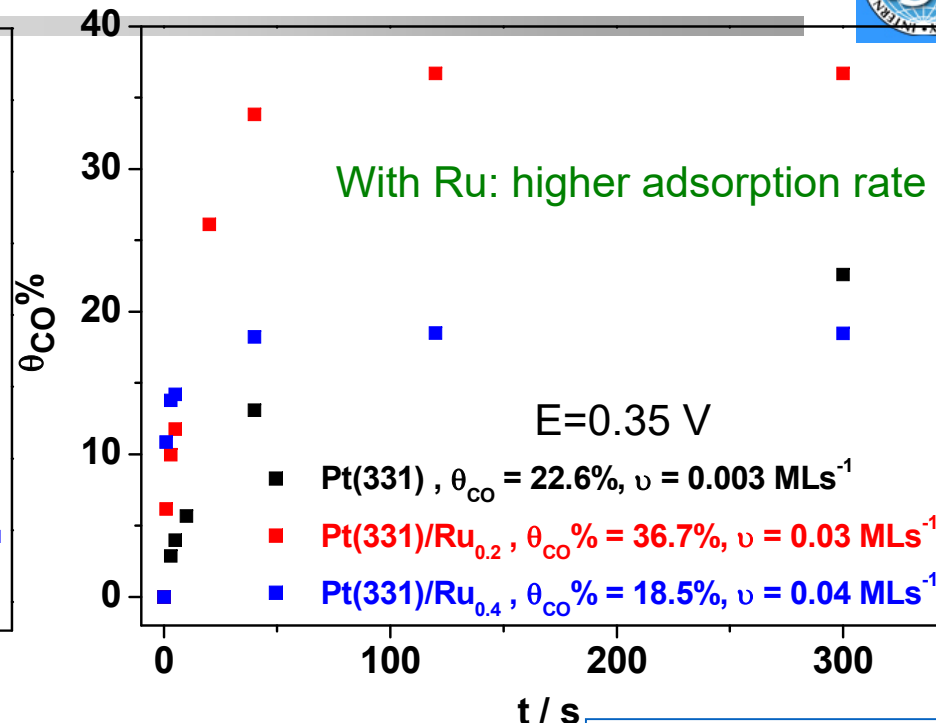
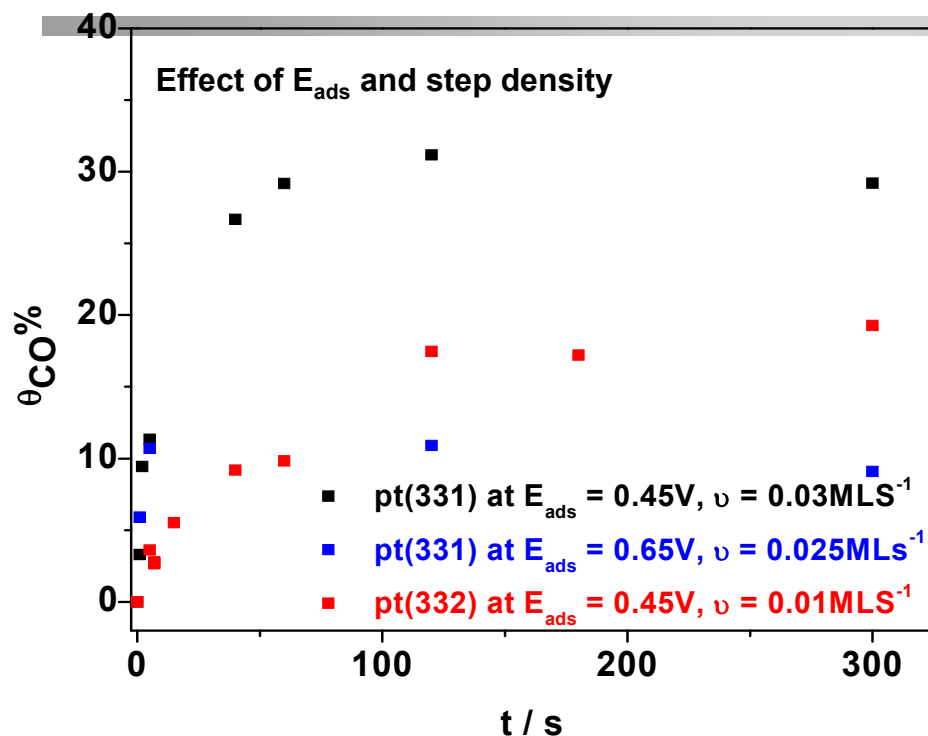


$$A_{CO_2} = \frac{z \cdot I_I(44)}{K^* \cdot I_F^{ges}}$$

18.05.2021

flow rate independence of CO<sub>2</sub> ==> CO<sub>2</sub> only from CO<sub>ad</sub>

# Effect of step density and Ru on the adsorption rates of methanol



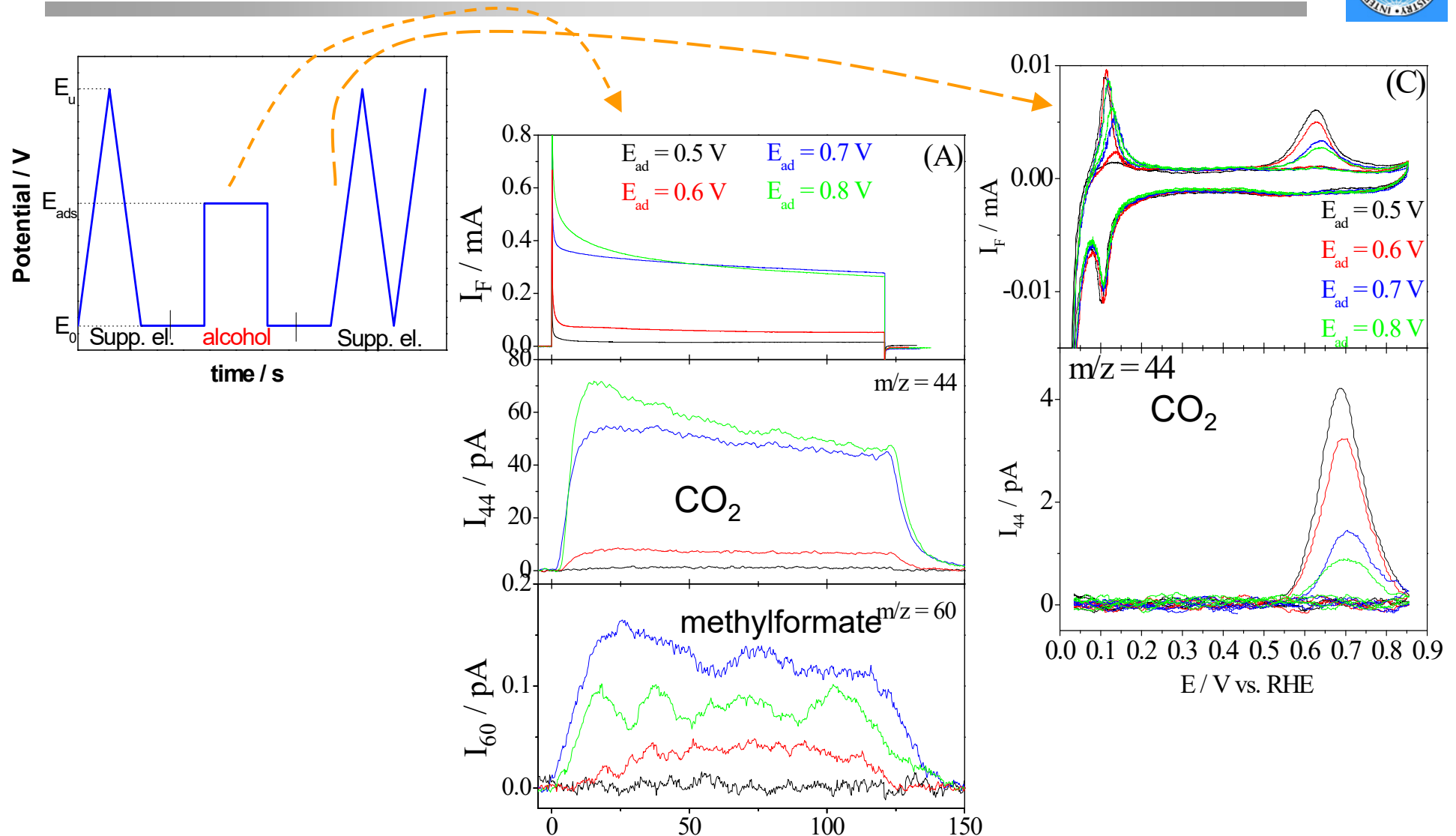
$$\nu = \frac{d\theta}{dt} = k(1-\theta)^x$$

$$\left. \frac{d\theta}{dt} \right|_{t=0} = k$$

$$\theta_{CO} = \frac{\Gamma_{CO}}{\Gamma_{CO}^{max}}$$

- The rate of methanol adsorption and oxidation is dependent on the step density and Ru coverage at step sites.
- Potential dependence: factor 10 per 100 mV

# Pt(331): MeOH current transients and adsorption rate

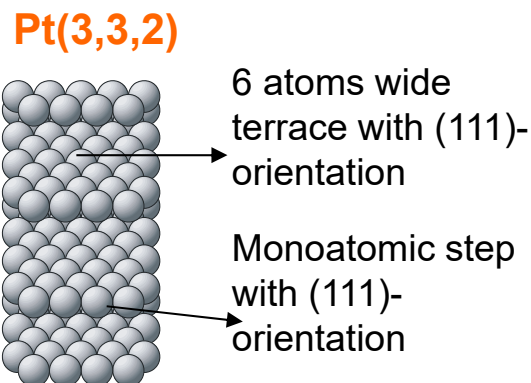
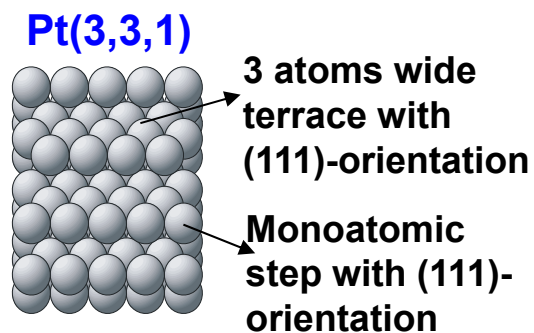
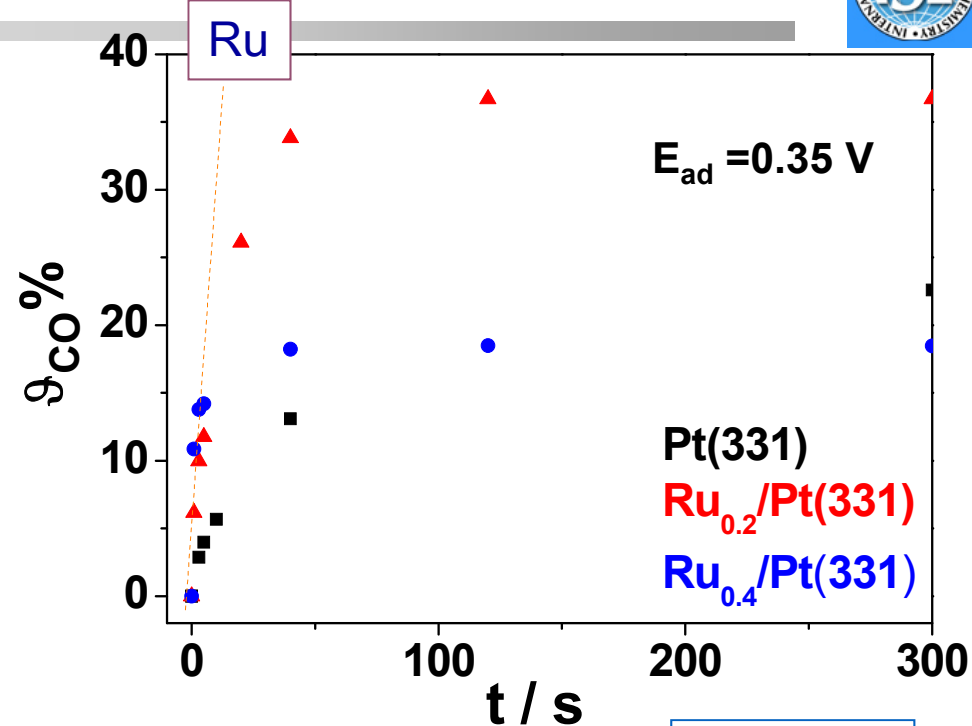
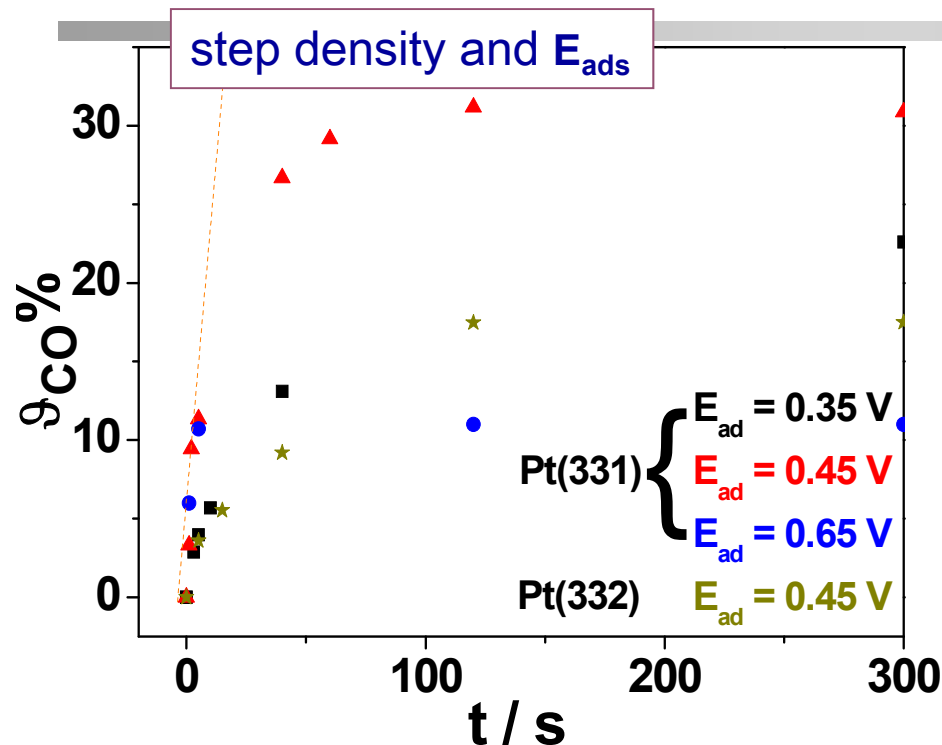


Pt(331) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution + (A) 0.1 M and (B) 0.01 M methanol after the step of the potential from 0.05 V to 0.5 V, 0.6 V, 0.7 V and 0.8 V. (C) Oxidation of methanol adsorbate formed from 0.1 M methanol with scan rate: 10 mVs<sup>-1</sup> and electrolyte flow rate: 2  $\mu$ Ls<sup>-1</sup>.

Mostafa, E.; Abd-El-Latif, A. A.; Baltruschat, H., *ChemPhysChem* **2014**, 15, 2029

Baltruschat, Jusys Tutorial: *Differential Electrochemical Mass Spectrometry*. 69<sup>th</sup> Annual ISE Meeting, 2-7.09.2018, Bologna, Italy

# Adsorption rates of methanol: Effect of ...



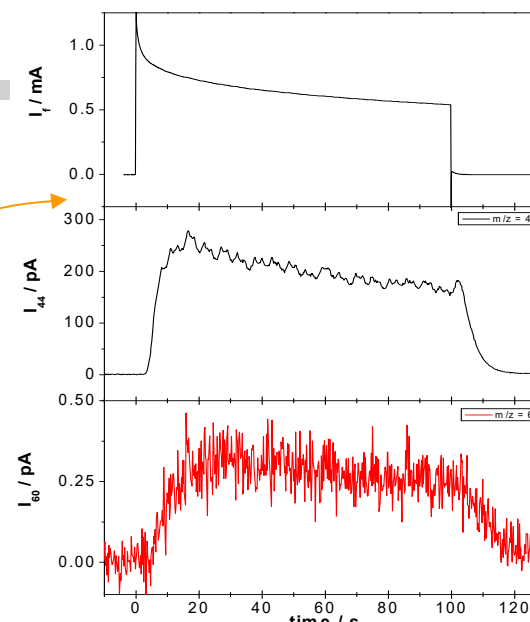
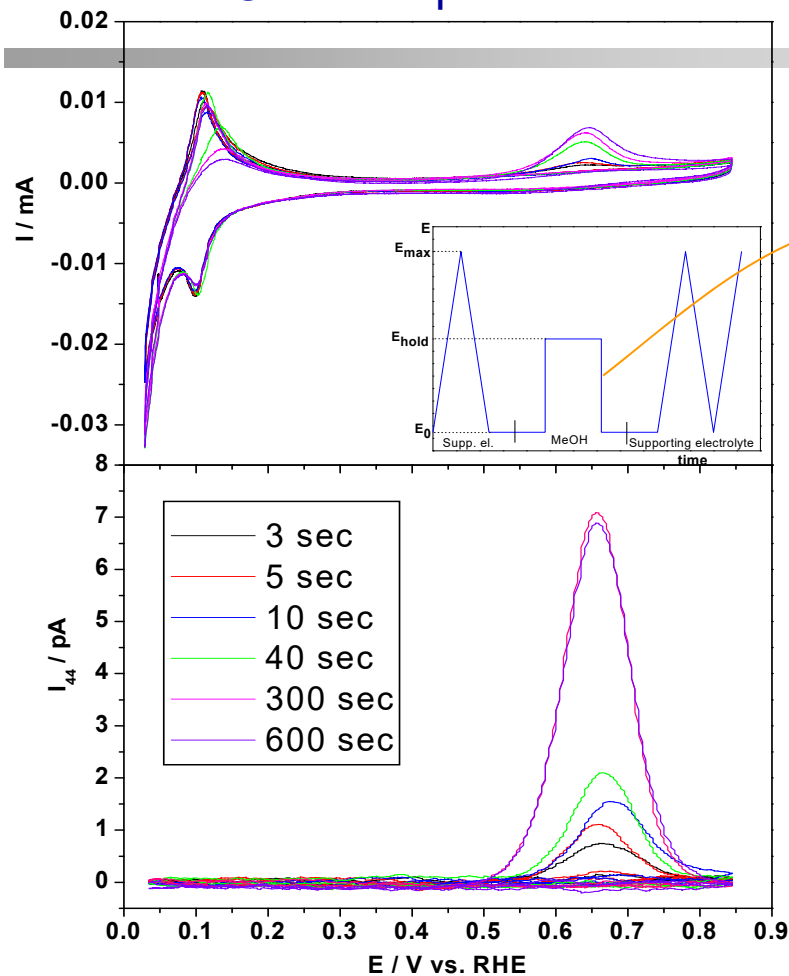
$$\theta_{CO} = \frac{\Gamma_{CO}}{\Gamma_{CO}^{max}}$$

$$v = \frac{d\theta}{dt} = k(1-\theta)^x$$

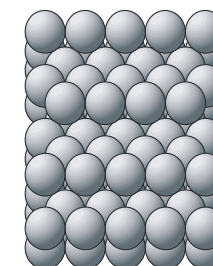
$$\left. \frac{d\theta}{dt} \right|_{t=0} = k$$

- The rate of methanol adsorption increases with step density and Ru coverage.
- Potential dependence: factor 10 per 100 mV  $\Rightarrow$  rds:  $\equiv C-H \rightarrow \equiv C. + H^+ + e^-$

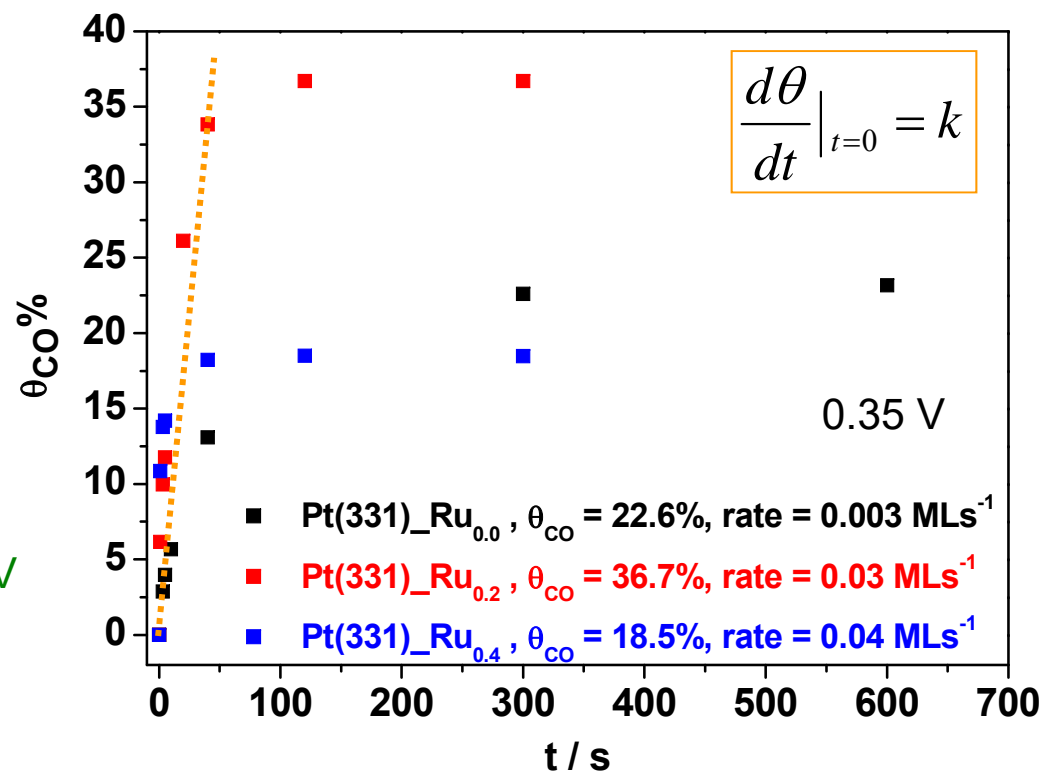
# MeOH adsorption rate



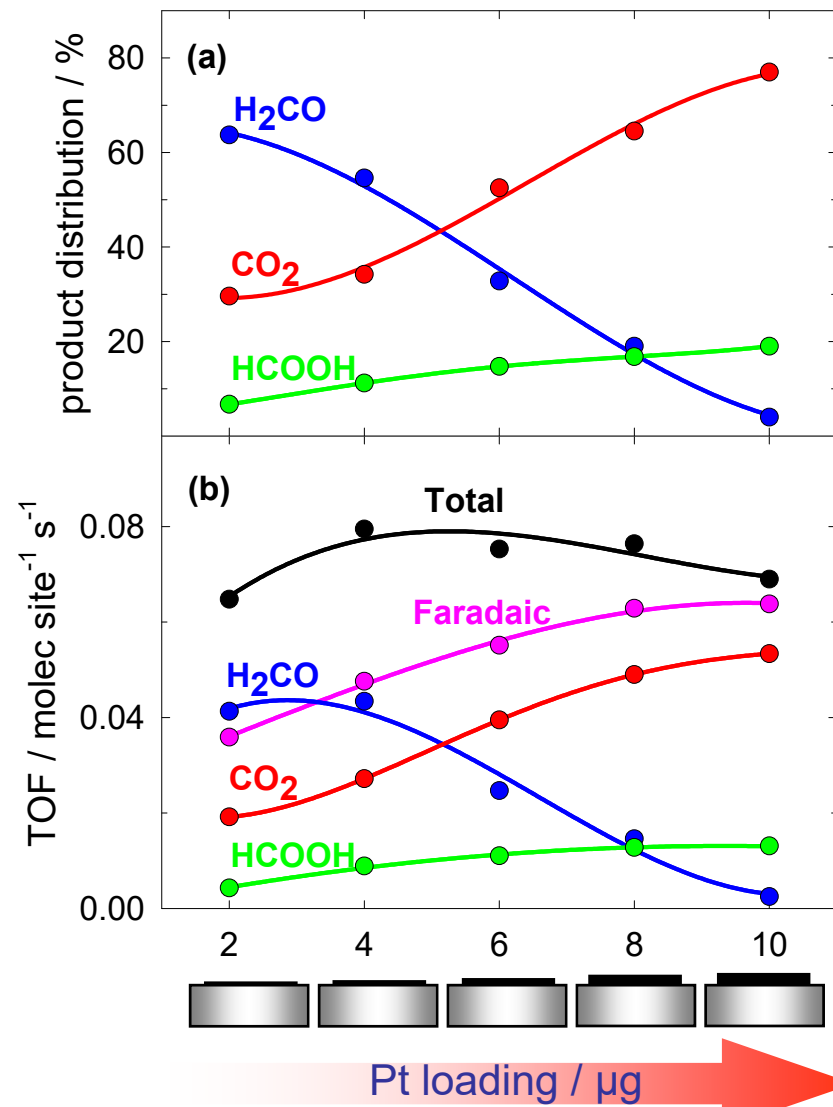
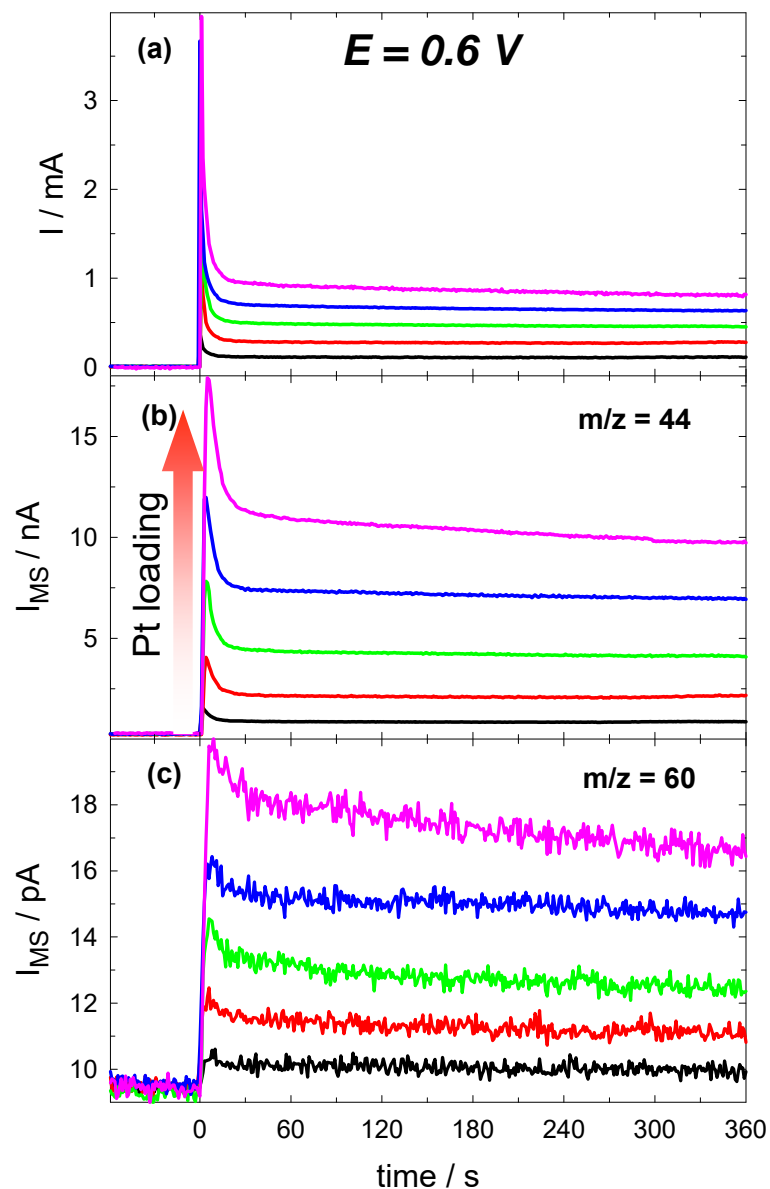
Pt(3,3,1)



- With Ru: higher adsorption rate
- The rate of methanol adsorption is doubled with doubled step density
- Potential dependence: factor 10 per 100 mV ==> 1st charge transfer is rds
- rate increases with increasing step density



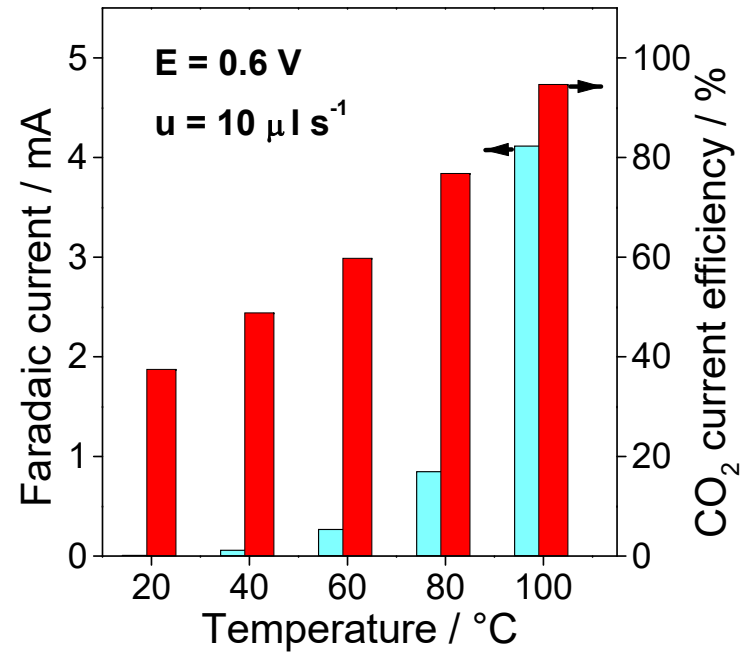
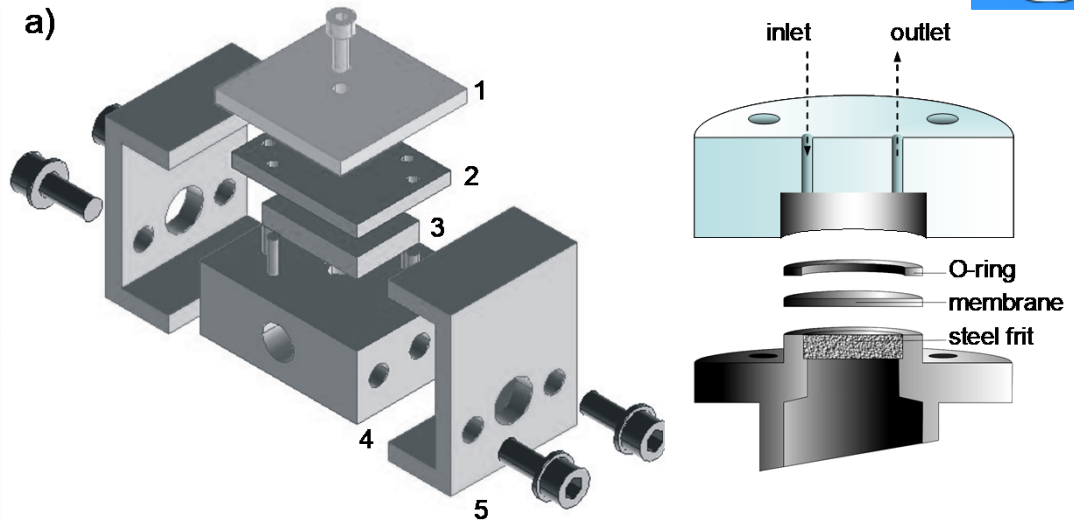
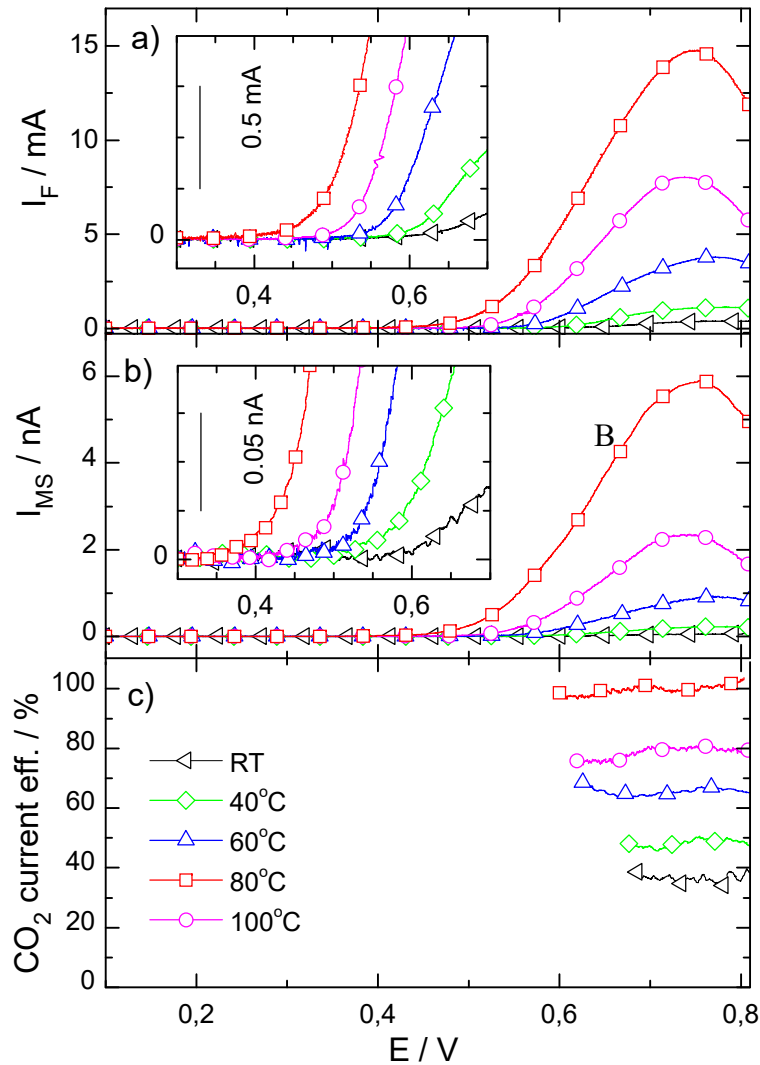
# Quantitative DEMS analysis of MOR product yields on Pt/C catalyst



➤ indirect detection of formic acid

Z. Jusys et al., Langmuir 19 (2003) 6759

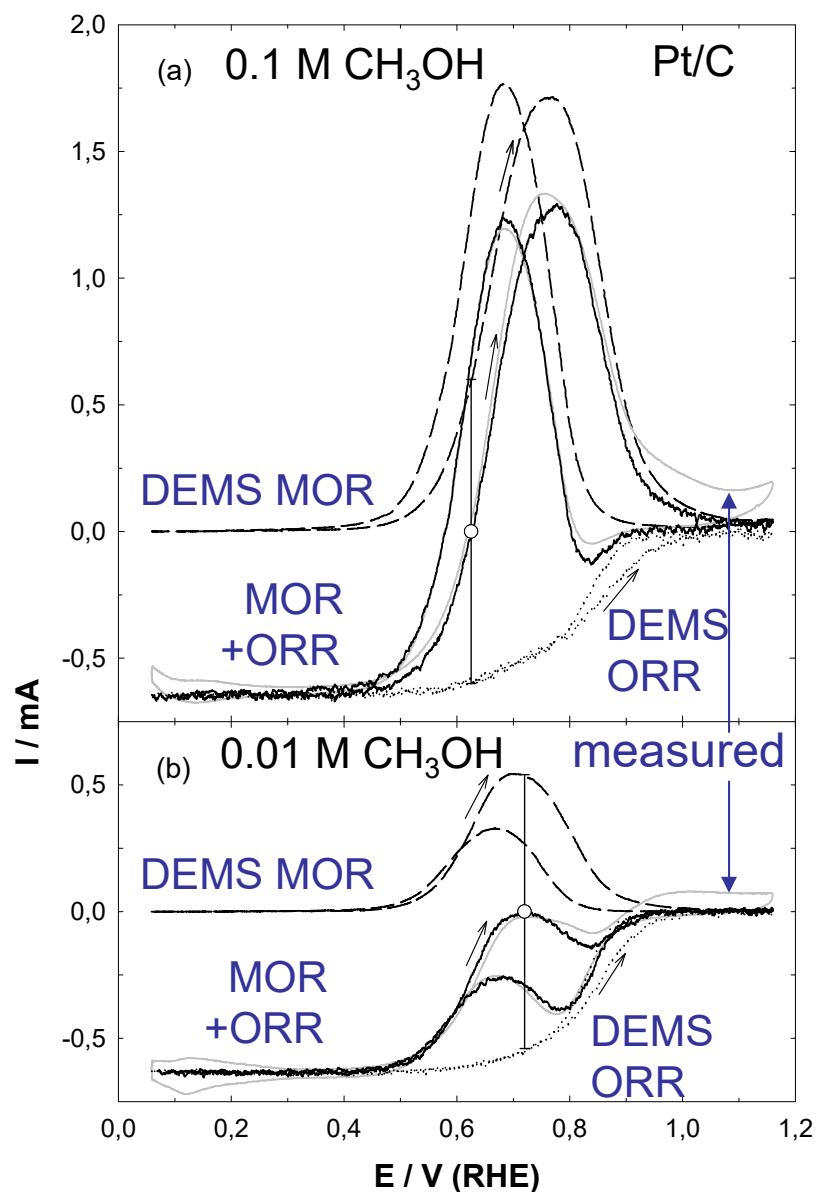
# Elevated temperature / pressure DEMS: fuel cell relevant conditions



- non-porous Teflon membrane (10 μm)
- 3 bar overpressure, up to 100 °C temperature

M. Chojak-Halseid *et al.*, JPCC 114 (2010) 22573

# Simultaneous MOR and ORR, flow cell: partial current deconvolution

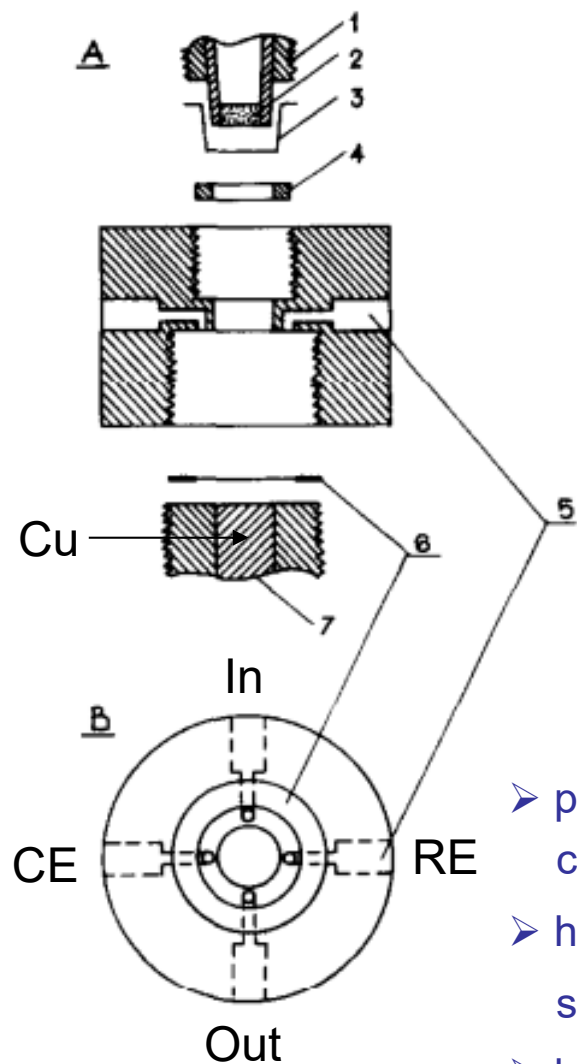


- measured current: MOR + ORR
- DEMS ORR:  $O_2$  consumption  $\times 4 / K^*$
- DEMS MOR:  $CO_2$  formation  $\times 6 / K^*$
- DEMS ORR + DEMS MOR = measured
- Mixed potential: DEMS ORR = DEMS MOR

Z. Jusys et al., EA 49 (2004) 3891

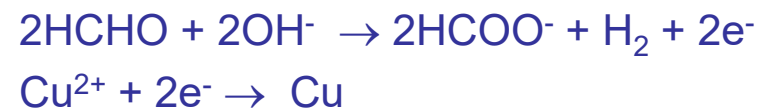
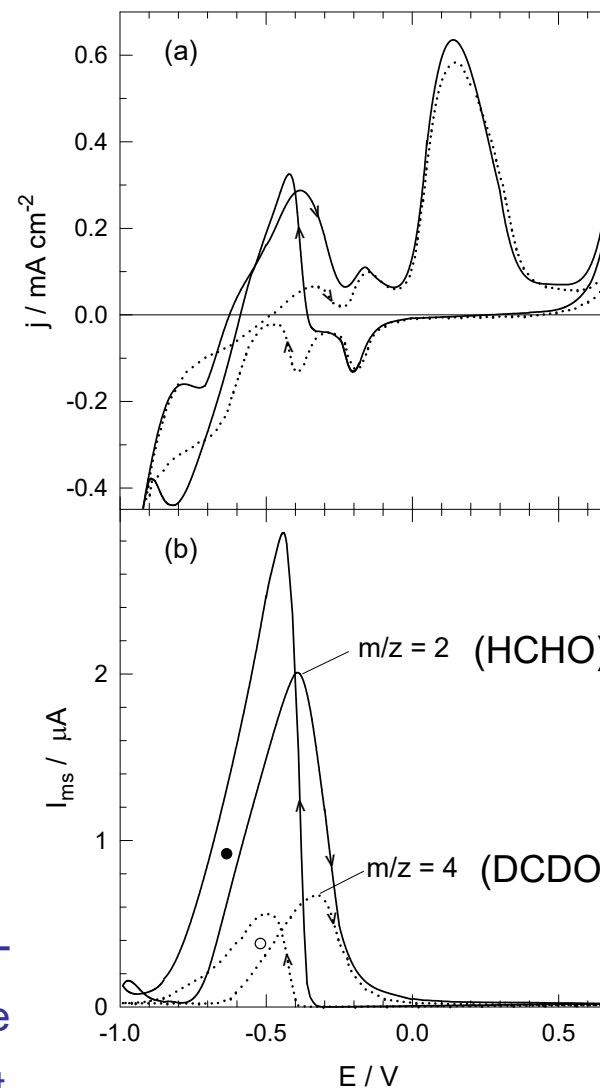


# DEMS flow cell: electroless copper deposition

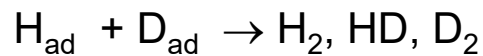
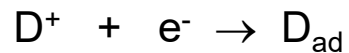
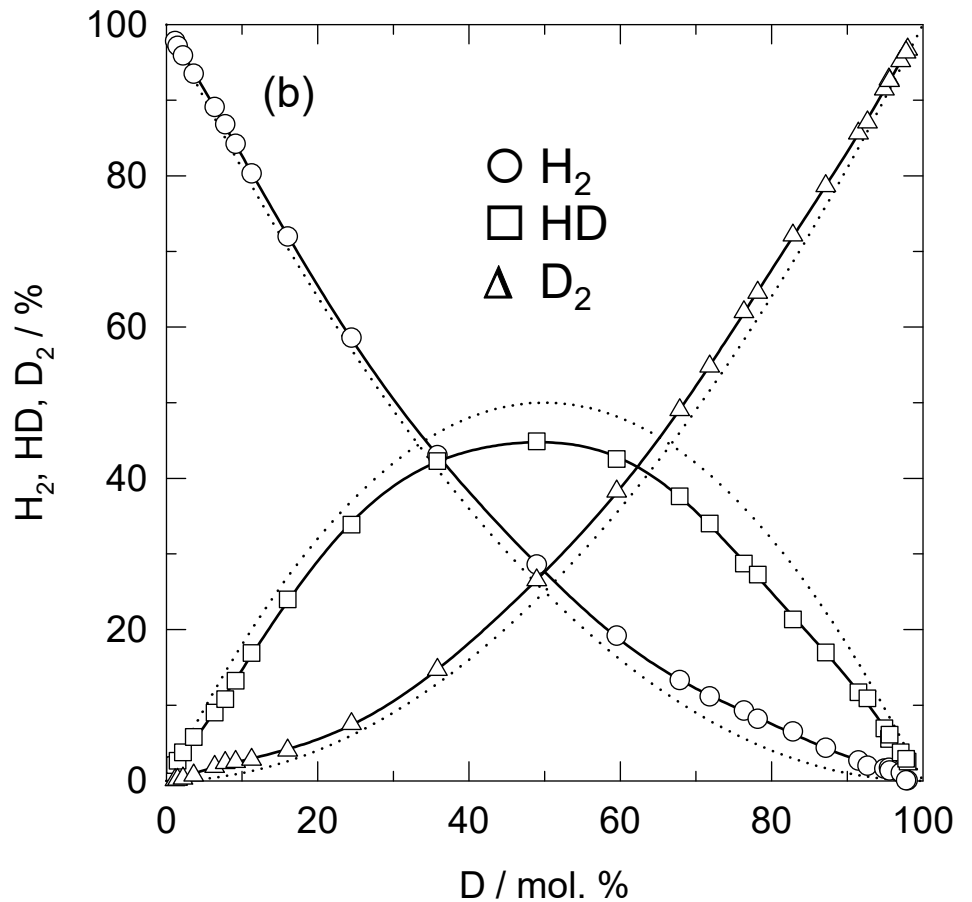
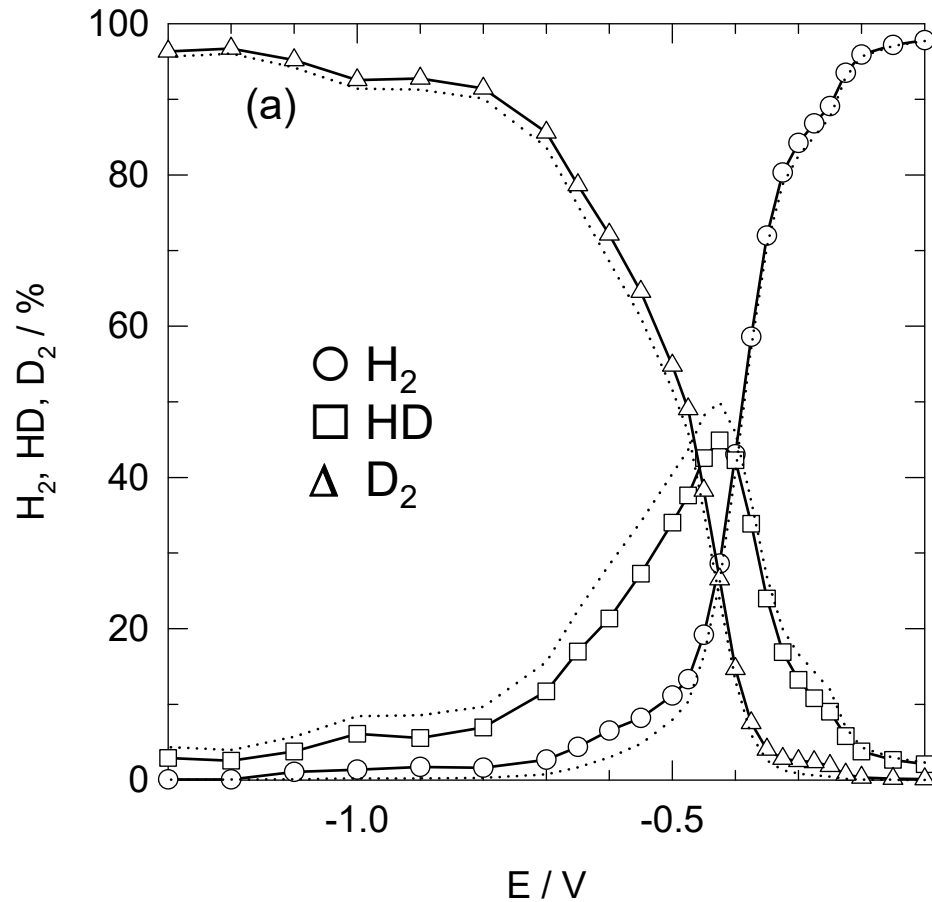


A.Vaškėlis, Z.Jusys,  
*Anal. Chim. Acta*  
 305 (1995) 227

- partial HCHO oxidation current monitored online
- hydrogen is formed exclusively from formaldehyde
- kinetic H/D isotope effect (C-H breaking in r.d.s.)



# „Classical“ DEMS cell: hypophospite oxidation on Ni in D<sub>2</sub>O at 80 °C

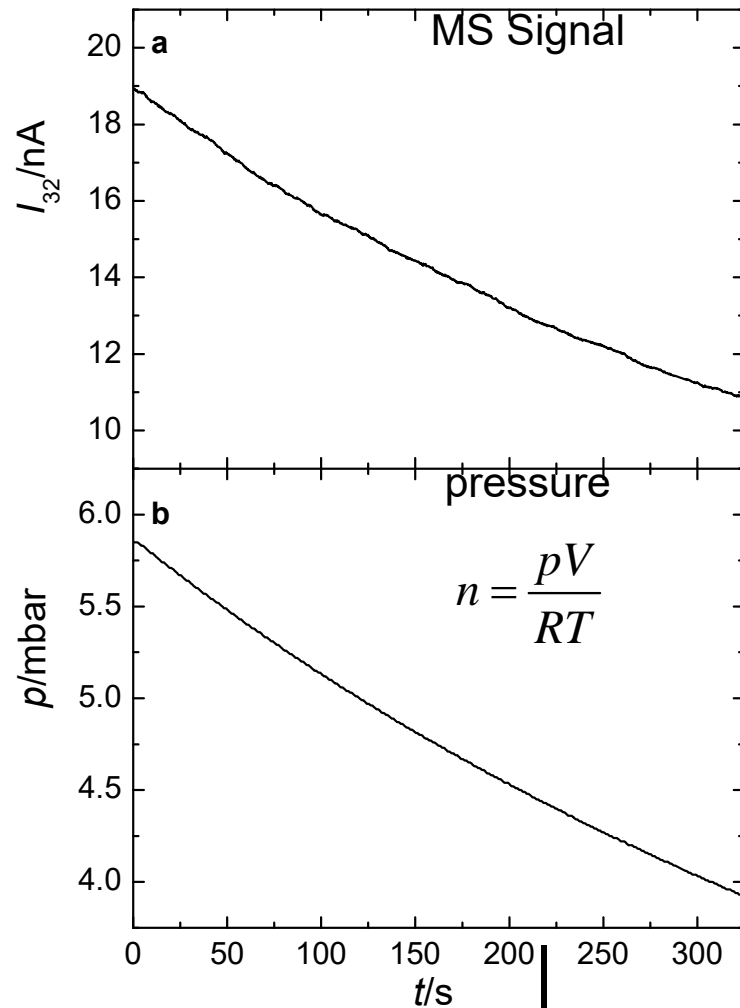


- potential dependent H<sub>2</sub>, HD, D<sub>2</sub> formation
- deviations from binomial distribution  
→ local H<sub>ad</sub> and D<sub>ad</sub> islands?

Expected: at the OCP: H/D = 1 (H<sub>2</sub>:HD:D<sub>2</sub> = 1:2:1)

Z. Jusys *et al.*, *Ber. Bunsenges. Phys. Chem.* 101 (1997) 1865

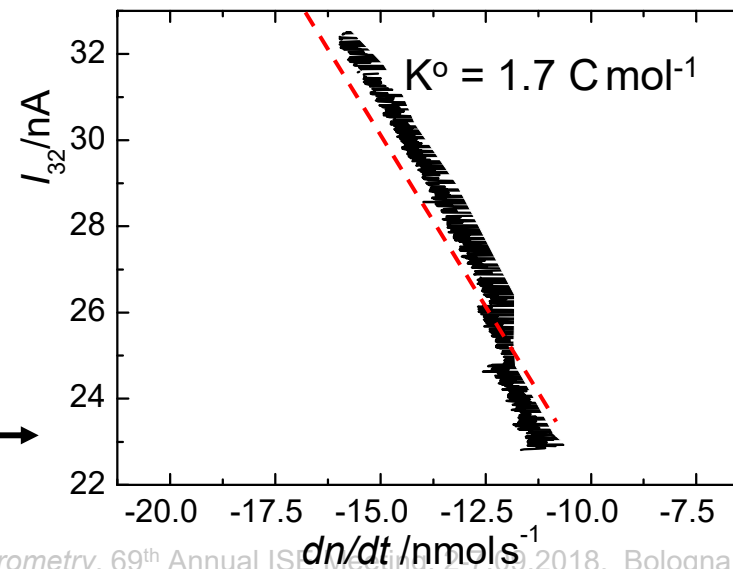
# Calibration Constant: $K^\circ$



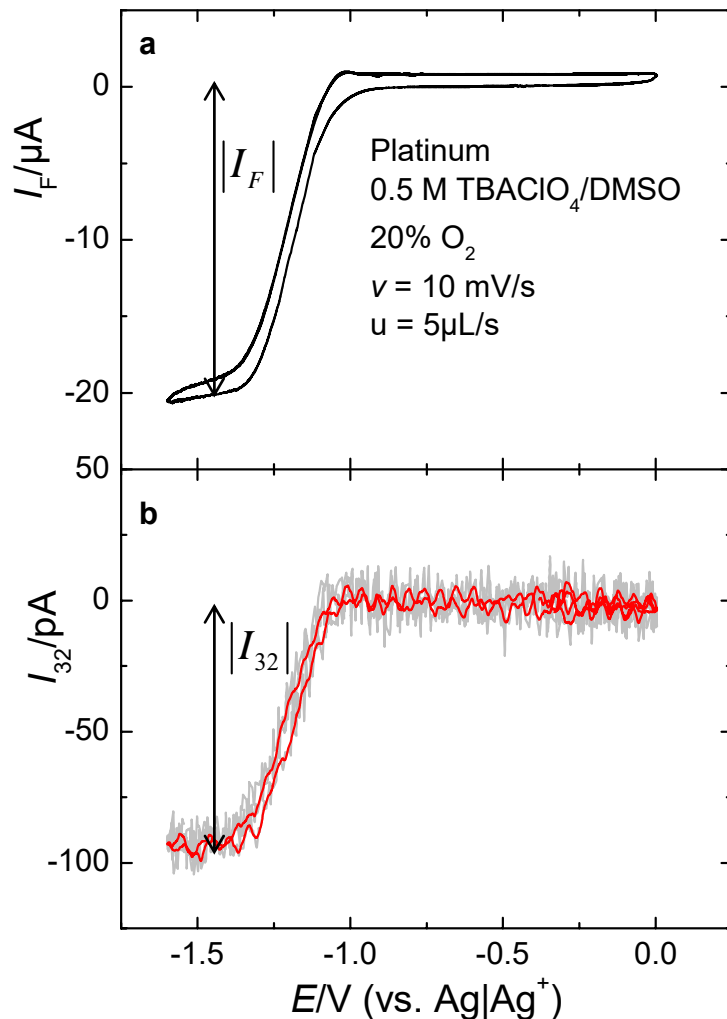
- $K^\circ$  is defined by the ratio of the measured ionic current  $I_i$  to the incoming flow of species  $J_i$ :

$$K^\circ = \frac{I_i}{J_i}$$

- $K^\circ$  is a function of all settings of the MS and the ionization probability of the analyte
- determination via calibration leak experiment:
  1. container of known volume filled with analyte
  2. MS is connected to the container via throttle valve
  3. incoming flux leads to MS signal and pressure decrease



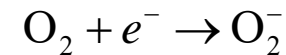
# Calibration Constant: $K^*$



- $K^*$  depends on the mass spectrometer **and** the cell set-up, i.e. its transfer efficiency  $N$

$$K^* = \frac{K^o \cdot N}{F}$$

- $K^*$  can conveniently be determined using a reaction of known stoichiometry, e.g. ORR the in DMSO/TBAClO<sub>4</sub>:



- $K^*$  is then be calculated from the ratio of the ionic current  $I_i$  to the Faradaic current  $I_F$

$$K^* = z \cdot \left| \frac{I_i}{I_F} \right|$$

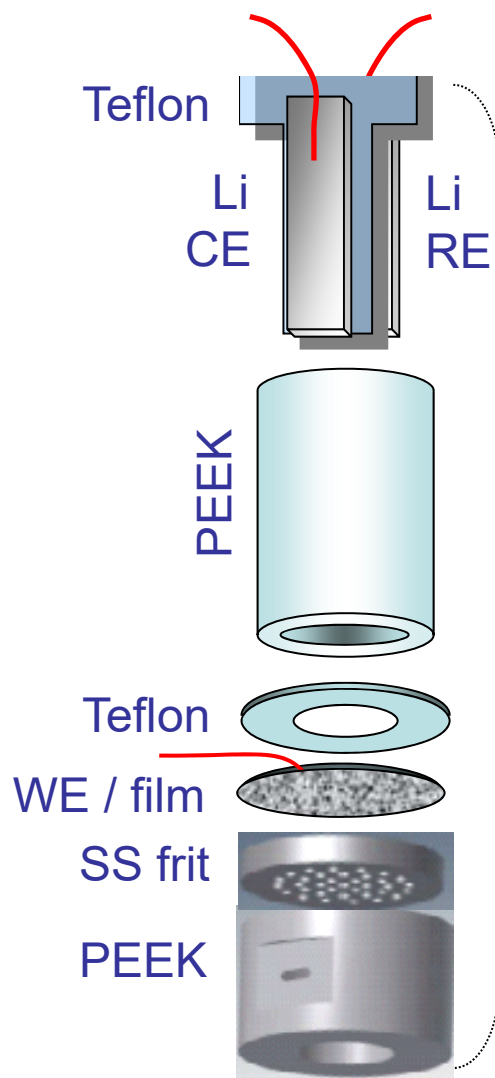
- For this case :  $I_F = -20 \mu\text{A}$   
 $I_{32} = -94 \text{ pA}$   
 $z = 1$

➤  $K^* = 4.7 \times 10^{-6}$

# Novel membrane inlet DEMS cell: "classical" design, aprotic electrolytes



## DEMS cell



➤ Simple, vacuum-tight design

< Teflon T-separator between Li counter & reference electrodes

< PEEK cylinder cell body (~0.5 ml)

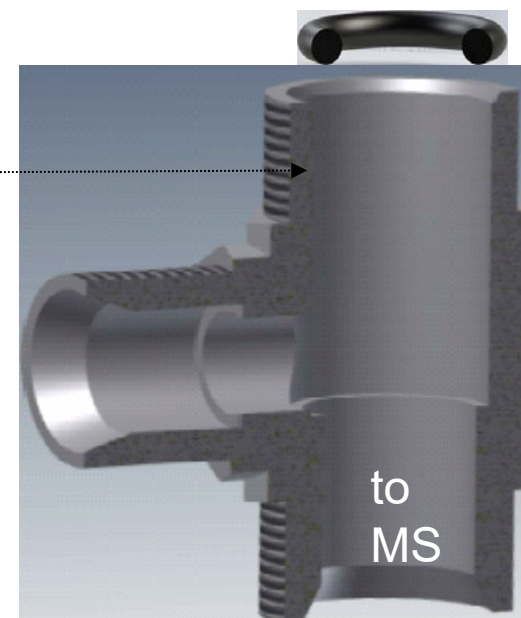
< Teflon gasket

< LMNO / Al / Teflon (FEP) film

< Stainless steel frit

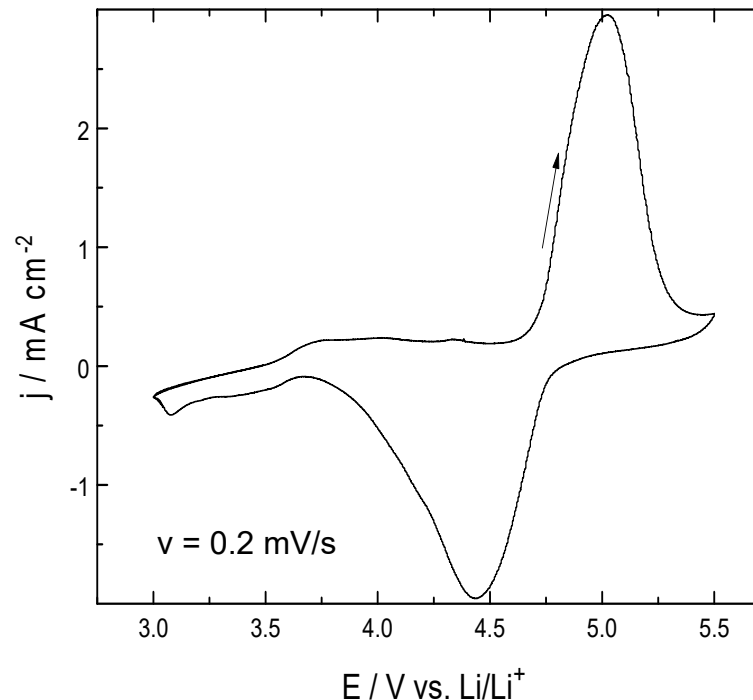
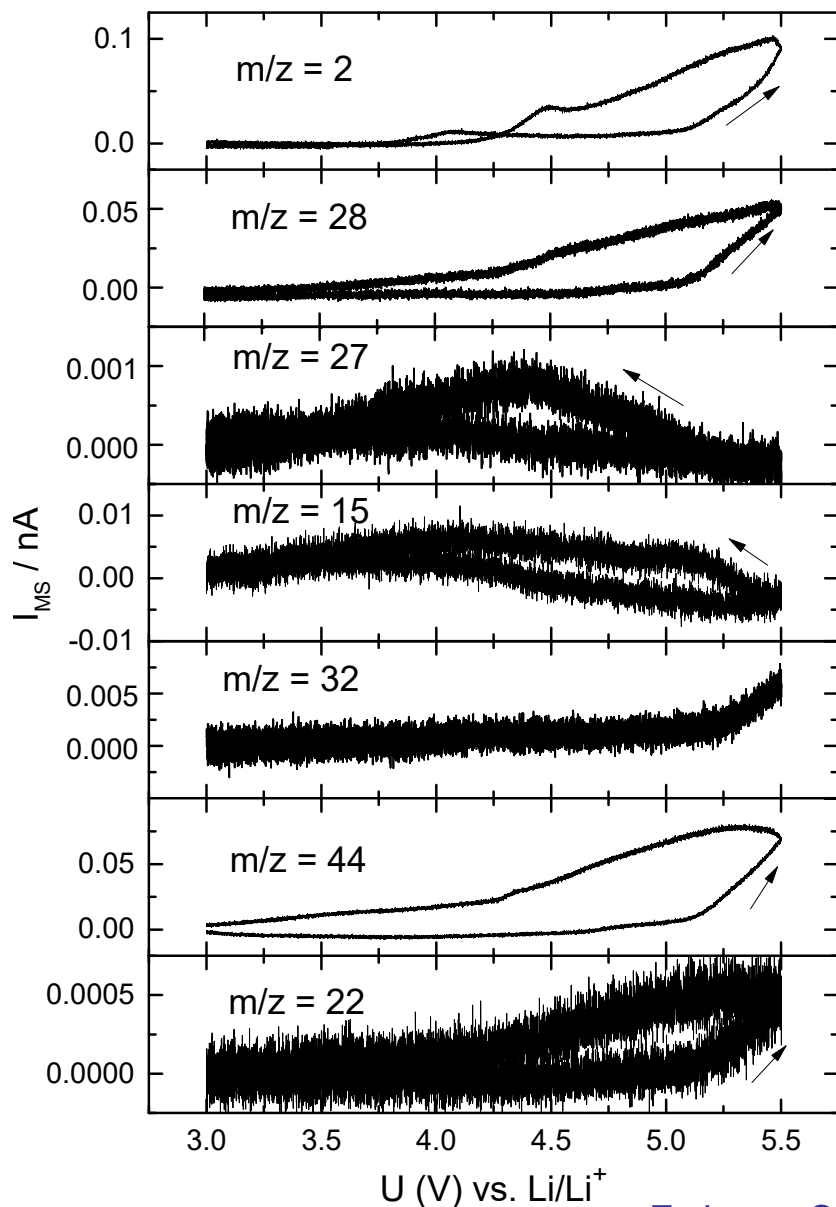
< PEEK cup cell body

## Swagelok housing



Z. Jusys, Symp 20, 9:45, 7th Sep

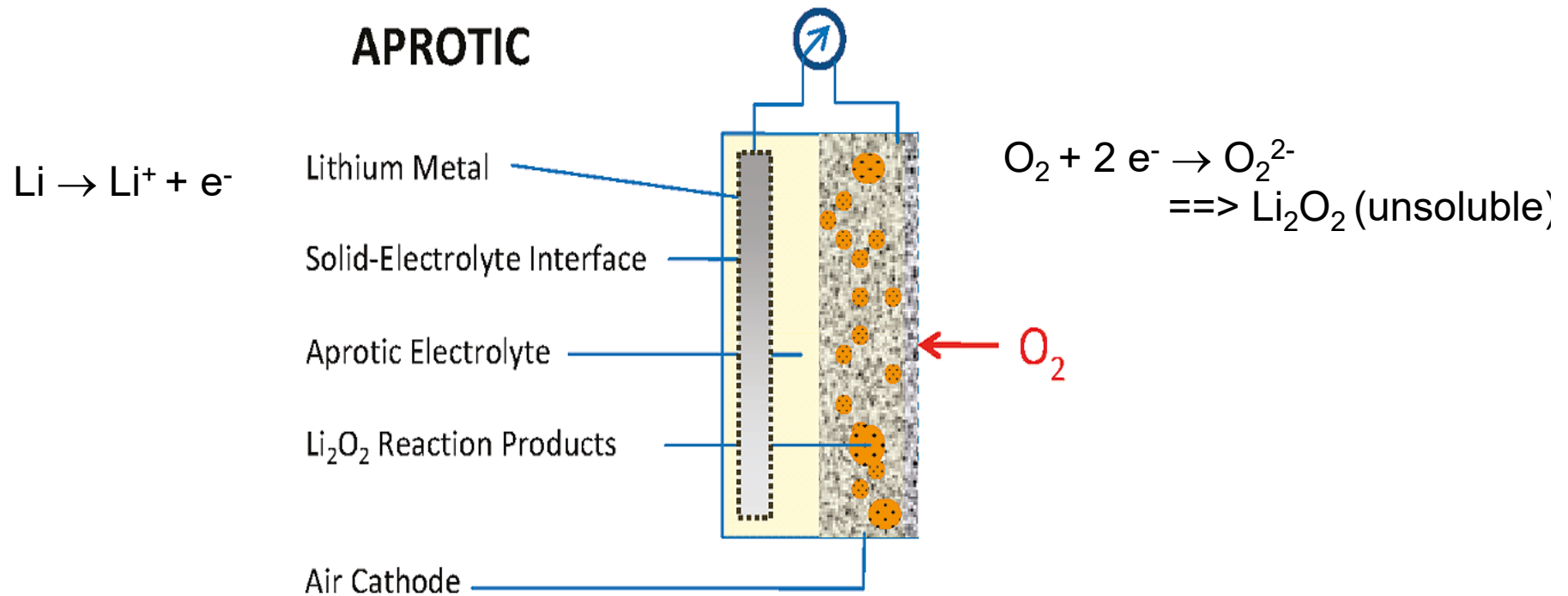
# Novel membrane inlet DEMS cell: high voltage LMNO cathode



Working electrode:  $\text{Li}_{(1+x)}\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  (Co-free)  
 Electrolyte: LP30 (1M LiPF<sub>6</sub>, 1:1 EC:DMC)  
 Membrane: non-porous FEP (50  $\mu\text{m}$ )

- Real cyclic voltammetry (not dQ/dt)
- Really differential (membrane inlet)
- Major gases: H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>
- Safety issues: H<sub>2</sub> + O<sub>2</sub> =

Z. Jusys, Symp 20, 9:45, 7th Sep



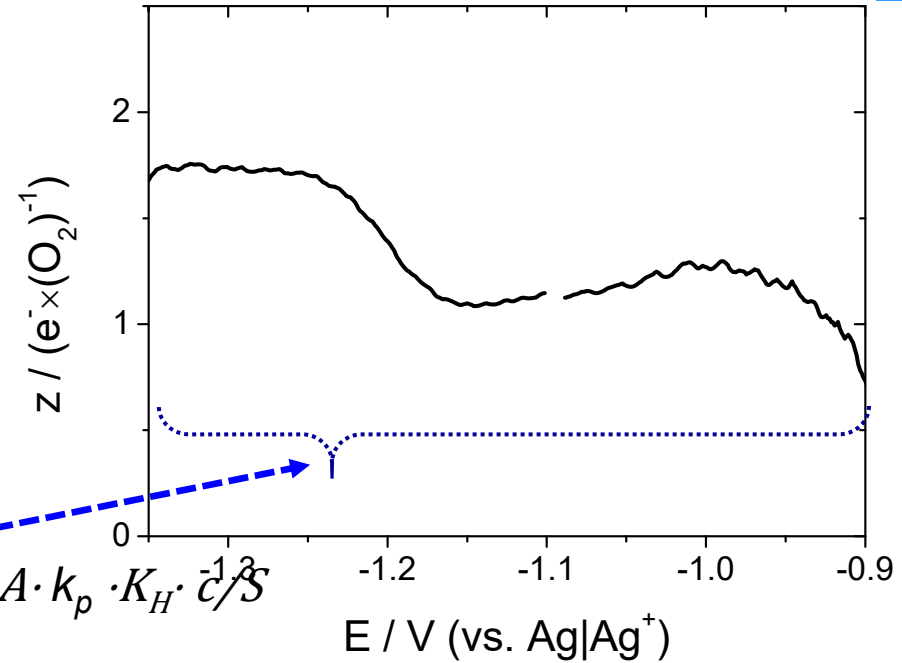
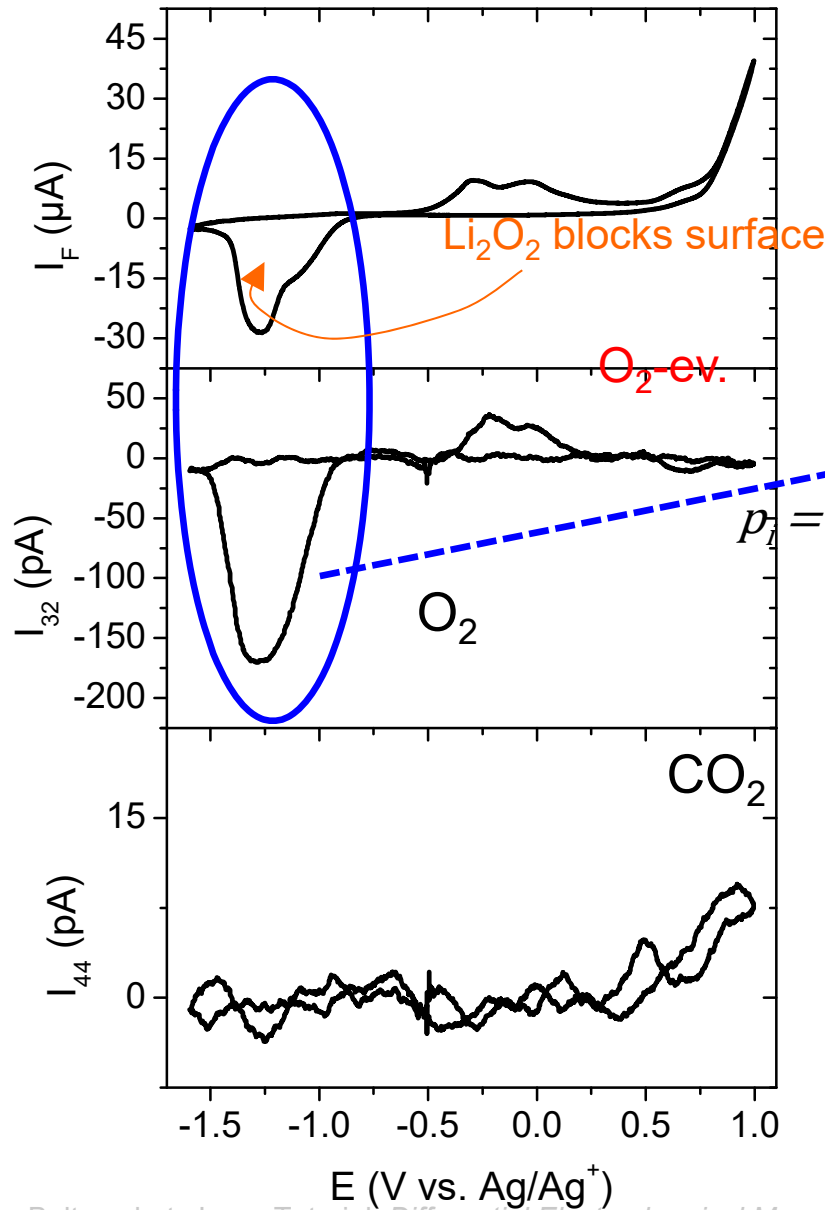
Advantage: at cathode no host for Li-ions needed (only C- electrode or catalyst)

Problems:

- unknown reactions in org. solvents
- 4 phases within  $\text{O}_2$  gas diffusion electrode:  
     electrolyte, catalyst, gasphase (air),  $\text{Li}_2\text{O}_2$  (insol, not conducting)
- uptake of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  from air

Girishkumar; McCloskey; Luntz; Swanson; Wilcke; *JPC Lett.* **2010**, 1, 2193

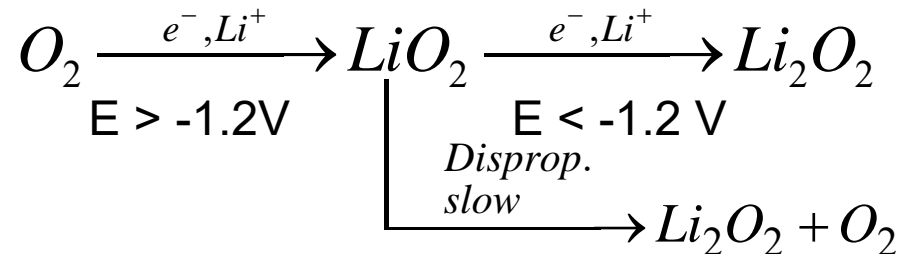
0.5 M LiClO<sub>4</sub> in DMSO purged with 20% O<sub>2</sub> in Ar



$$p_1 = RTA \cdot k_p \cdot K_H \cdot \bar{c} / S$$

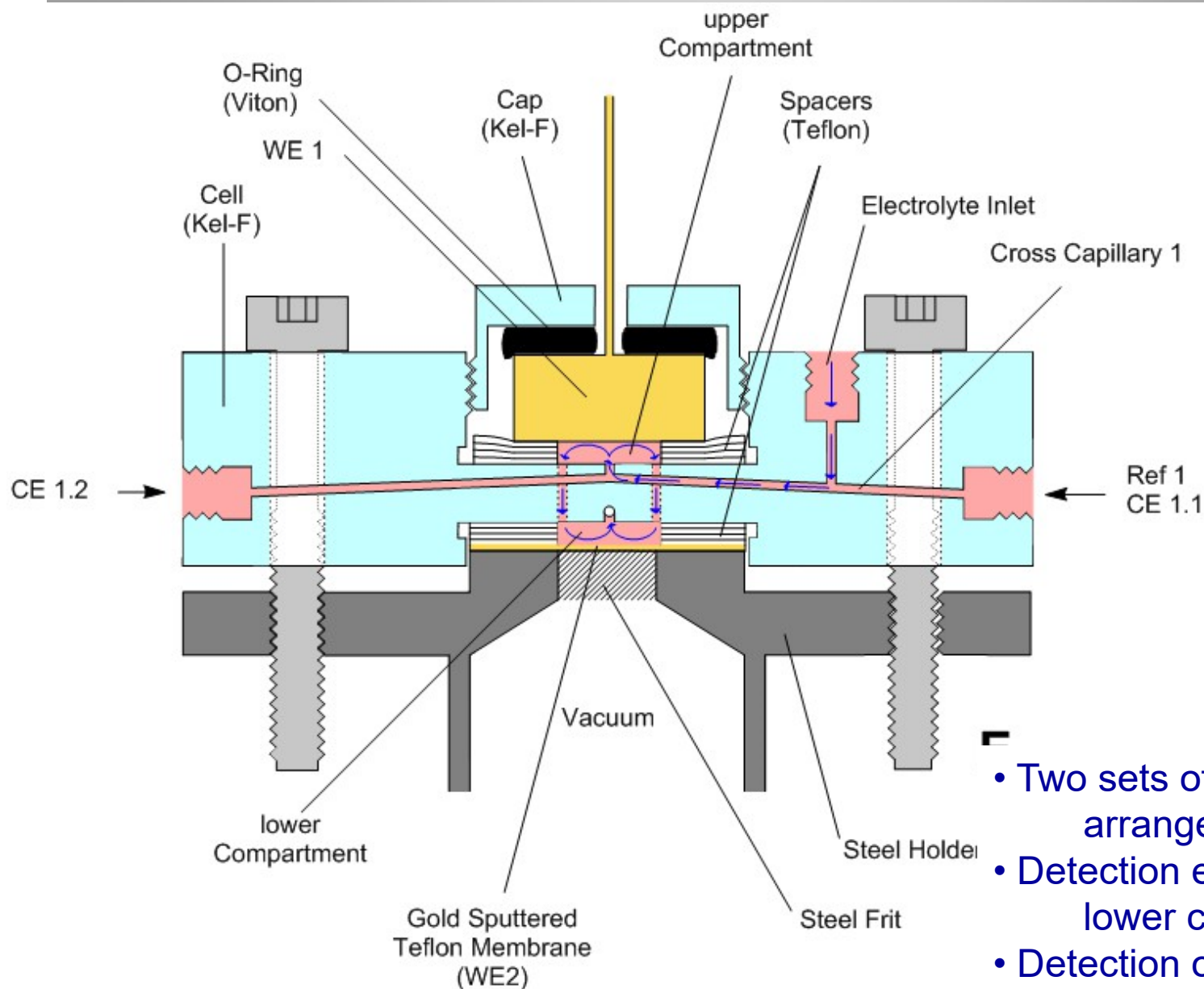
**Low  $\eta$ :** - Indirect pathway: superoxide formation  
 - Disproportionation to peroxide slow  
 (superoxide survives transfer from the 1st to the 2nd compartment)

**Large  $\eta$ :** Direct electrochem. peroxide formation

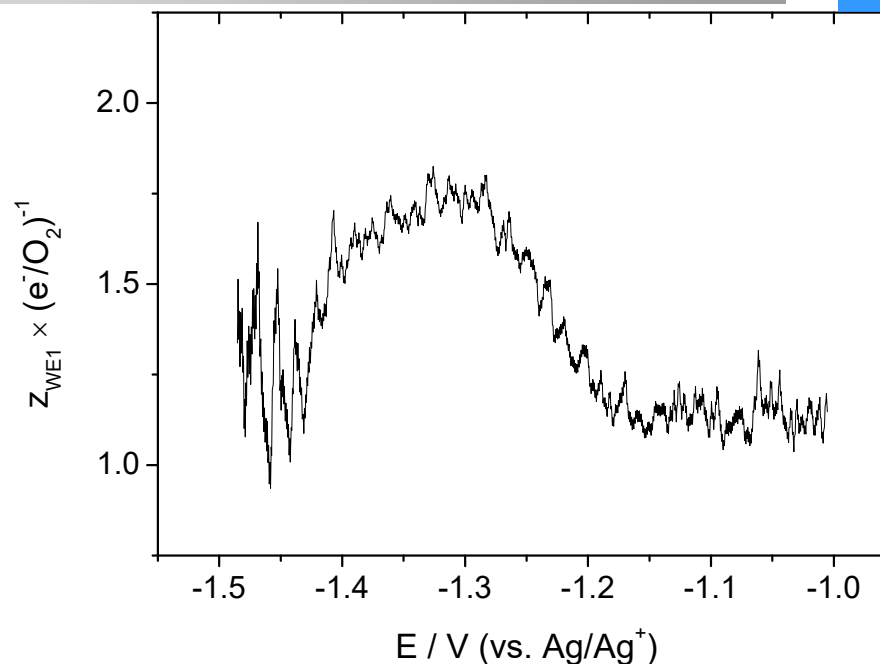
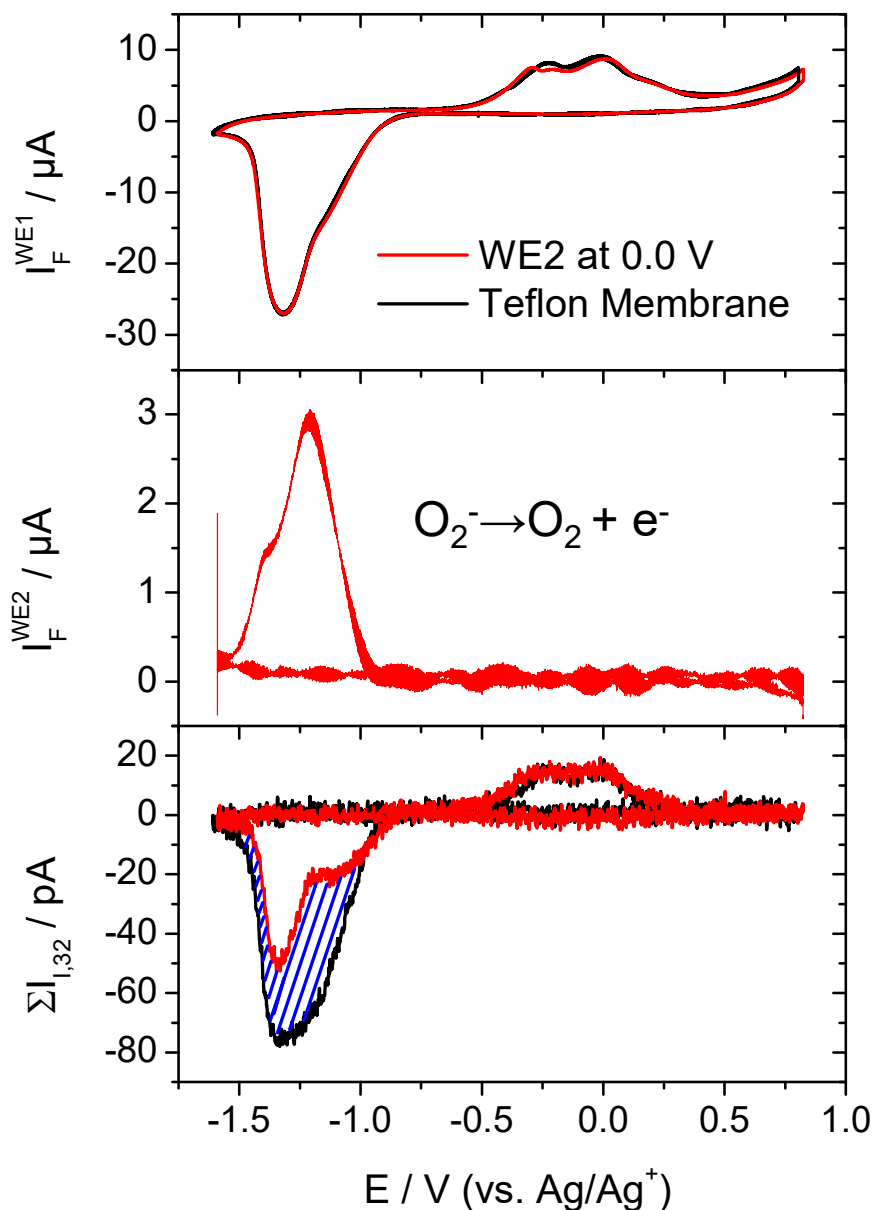




# Aprotic systems



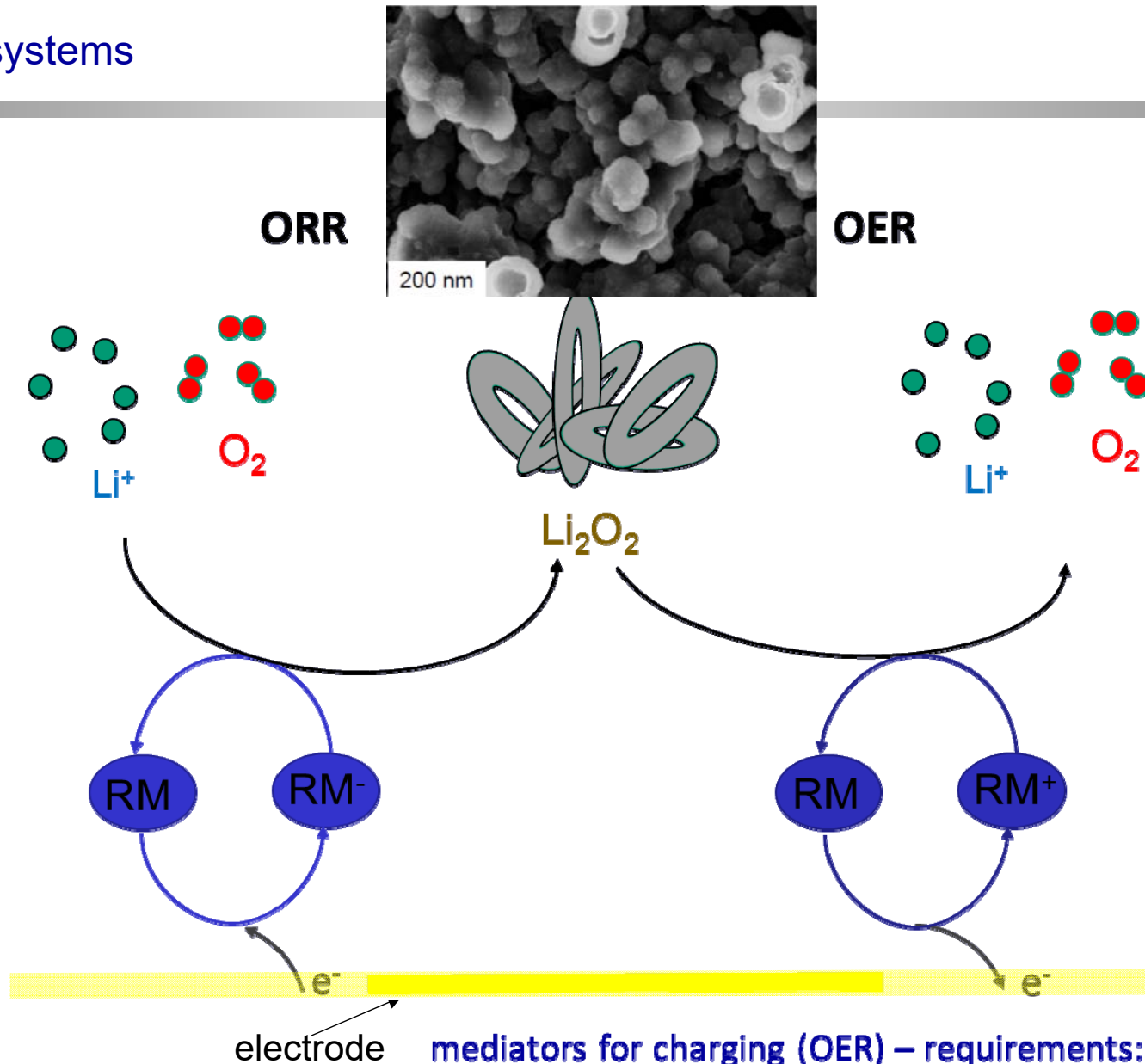
- Two sets of 3-electrode arrangements
- Detection electrode in lower compartment
- Detection of reaction products of 1<sup>st</sup> and 2<sup>nd</sup> electrode: MS



$$I_{I,32}^{WE1} = K_1^* \cdot \frac{I_F^{WE1}}{z_{WE1}}$$

Black curves yield:  
 Number of electrons transferred per reduced molecule of oxygen

Difference of ionic current yields  
 Ionic current due to reaction at WE2 ...



electrode

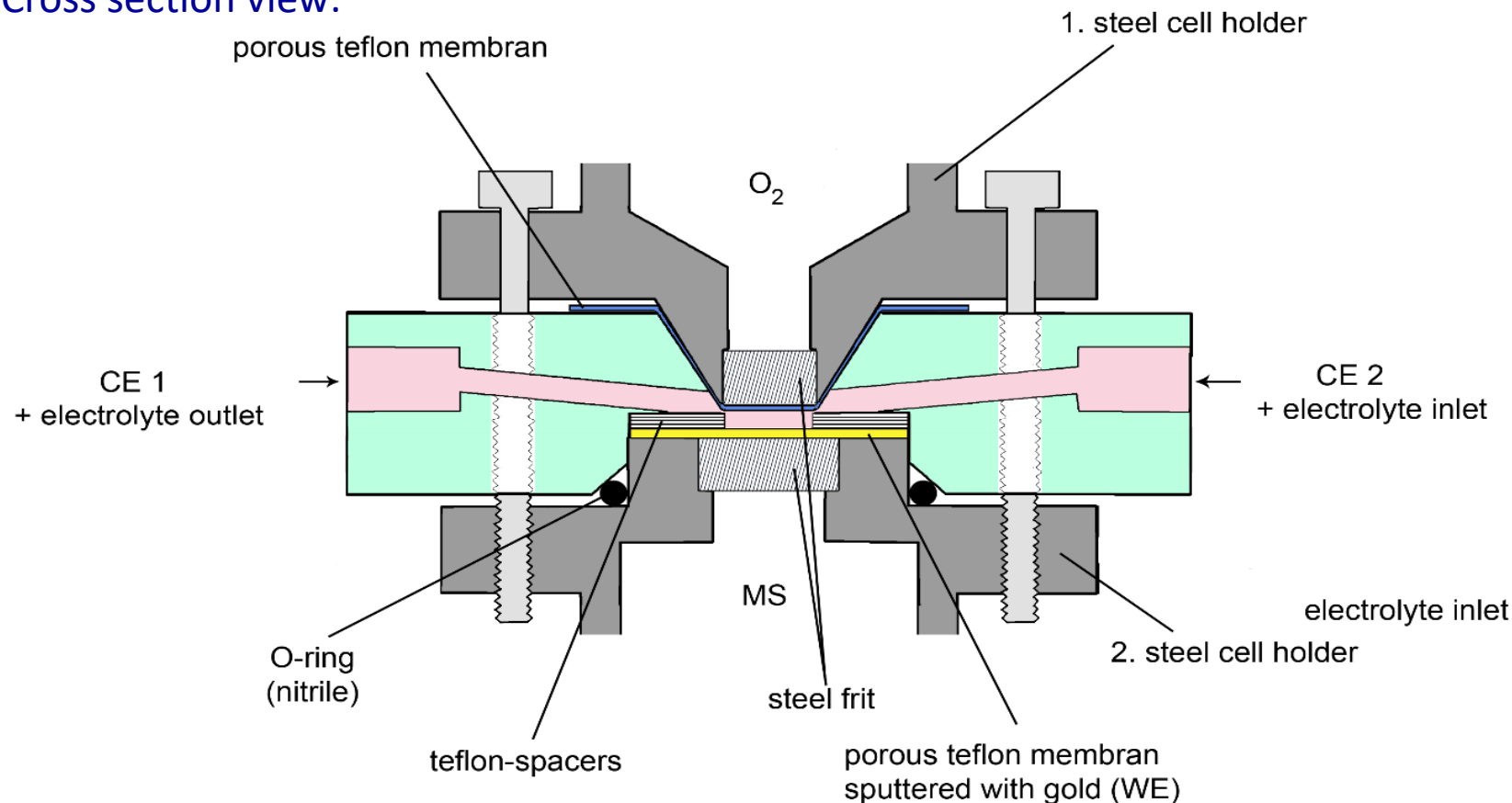
mediators for charging (OER) – requirements:

- redoxpotential below charging pot. of Li-O<sub>2</sub> (max 4.5 V)
- electrolyte is stable towards RM und RM<sup>+</sup>
- RM and RM<sup>+</sup> are stable towards O<sub>2</sub>

# Design of the thin layer cell



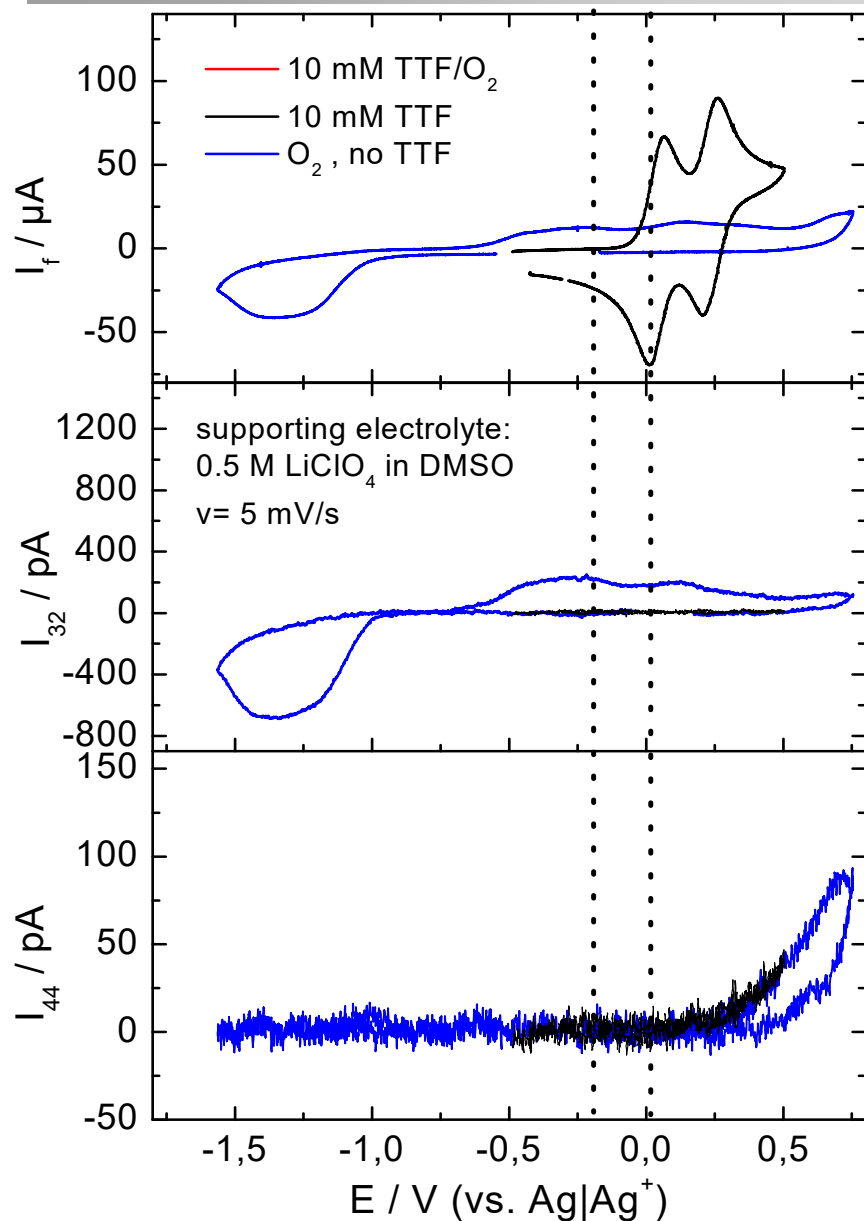
## Cross section view:



- Thin layer DEMS-cell with in-situ  $O_2$  saturation of the WE-compartment.
- Electrolyte volume in WE-compartment:  $5 \mu\text{L}$ .
- **Electrode area to electrolyte volume ratio comparable to batteries.**
- **Confined volume to investigate the influence of redox mediators.**
- There is no flux of electrolyte through the cell during the experiments.

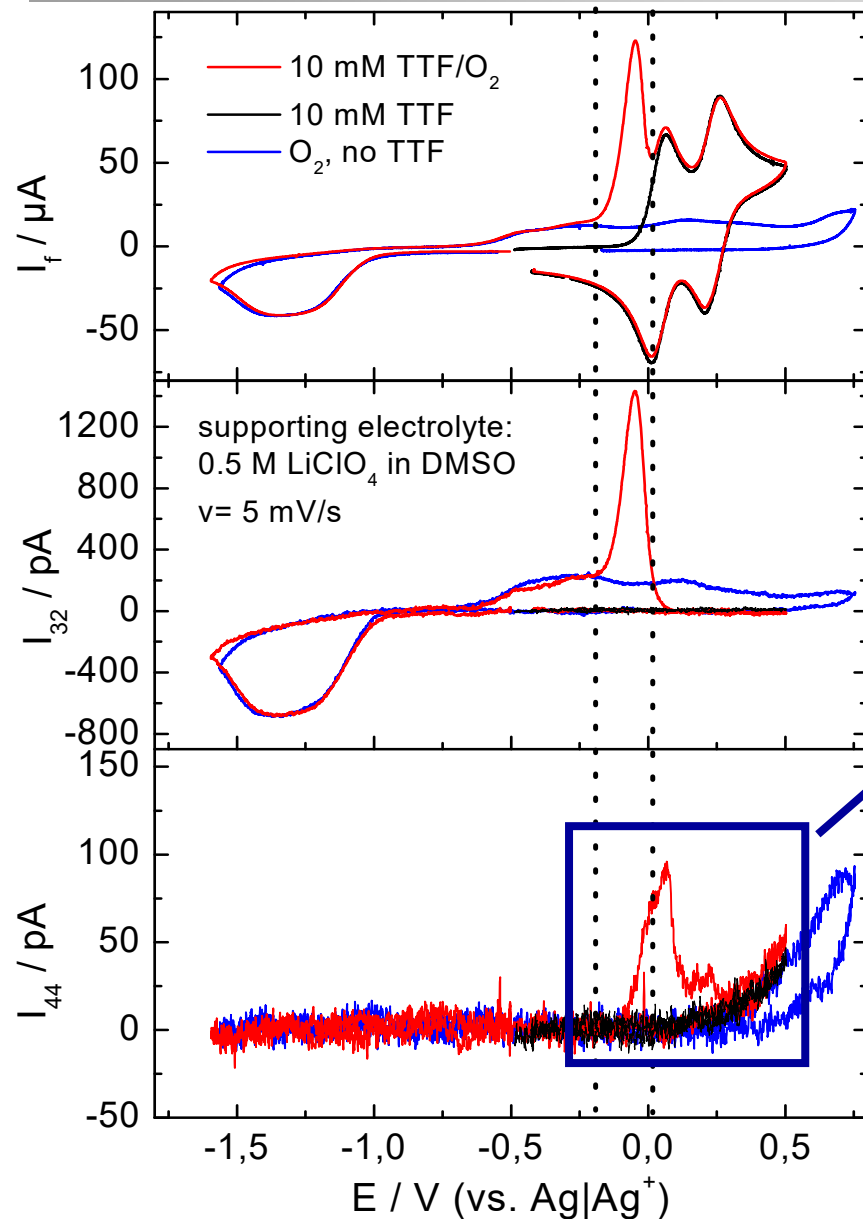
Bawol, P. P.; Reinsberg, P.; et al., *PCCP* **2018**, 20, 21447

Baltruschat, Jussy Tutorial: *Differential Electrochemical Mass Spectrometry*. 69<sup>th</sup> Annual ISE Meeting, 2-7.09.2018, Bologna, Italy



ORR and OER at Au in thin layer cell

0.5 M LiClO<sub>4</sub> with 10 mM TTF

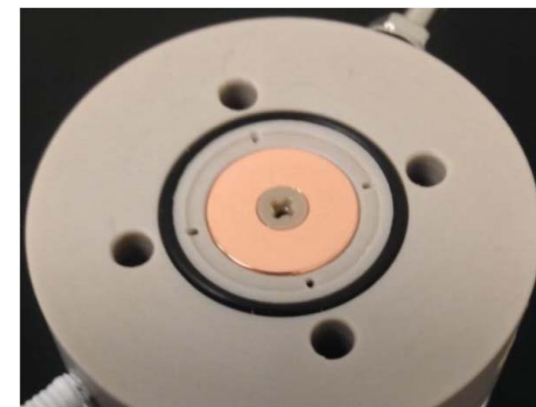
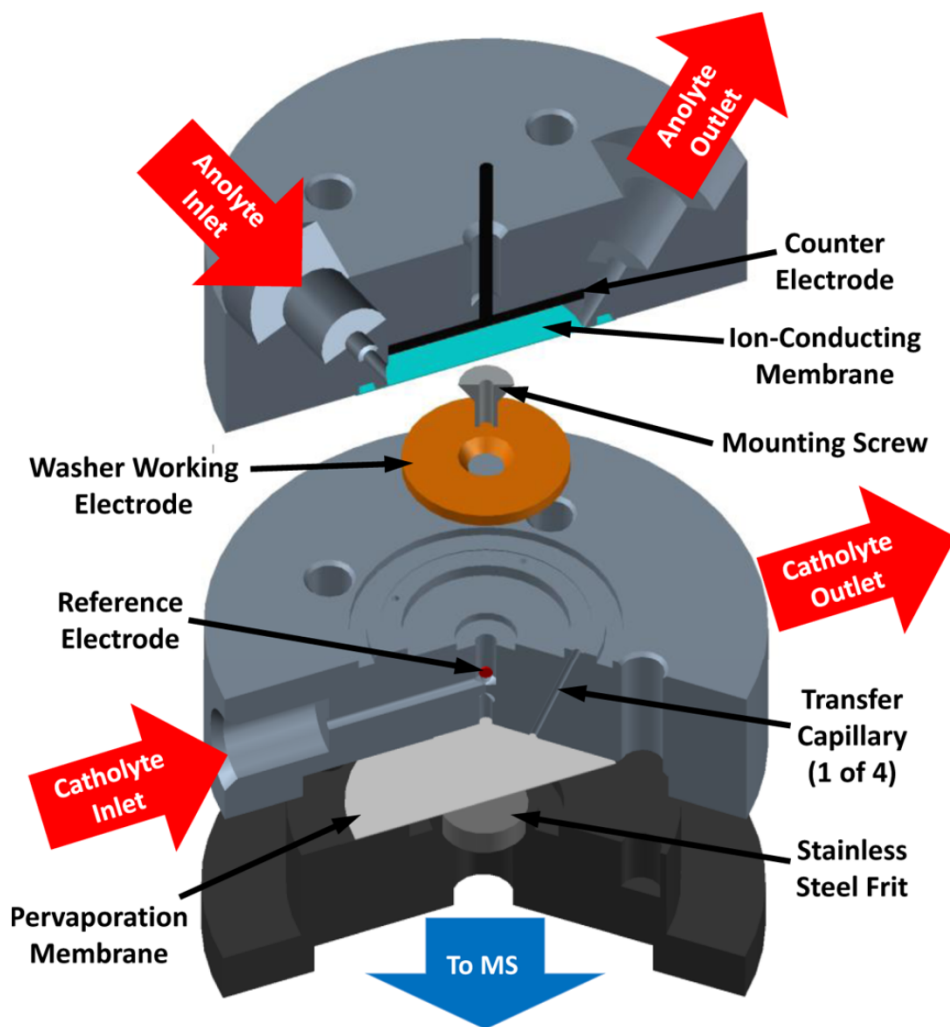


## ORR and OER at Au in thin layer cell

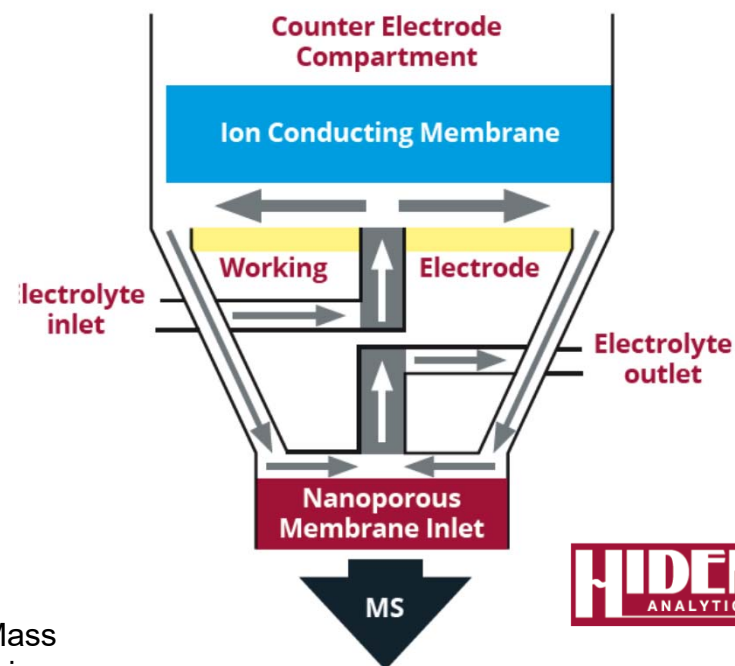
0.5 M LiClO<sub>4</sub> with 10 mM TTF

### O<sub>2</sub> + TTF

- An additional Peak in OER region (CVs and MSCV of mass 32)  
 → Activity of the RM towards Li<sub>2</sub>O<sub>2</sub> oxidation.
- After the OER has finished the CV follows the CV of the TTF-redox couple
- Additional CO<sub>2</sub> evolution!  
 → Carbon source is in that case TTF, because for the supporting electrolyte there is no CO<sub>2</sub> evolution in this region.



**Type B DEMS cell for electrochemical reaction studies**



Clark, E. L.; Singh, M. R.; Kwon, Y.; Bell, A. T., Differential Electrochemical Mass Spectrometer Cell Design for Online Quantification of Products Produced during Electrochemical Reduction of CO<sub>2</sub>. *Analytical Chemistry* **2015**, *87*, (15), 8013-8020.

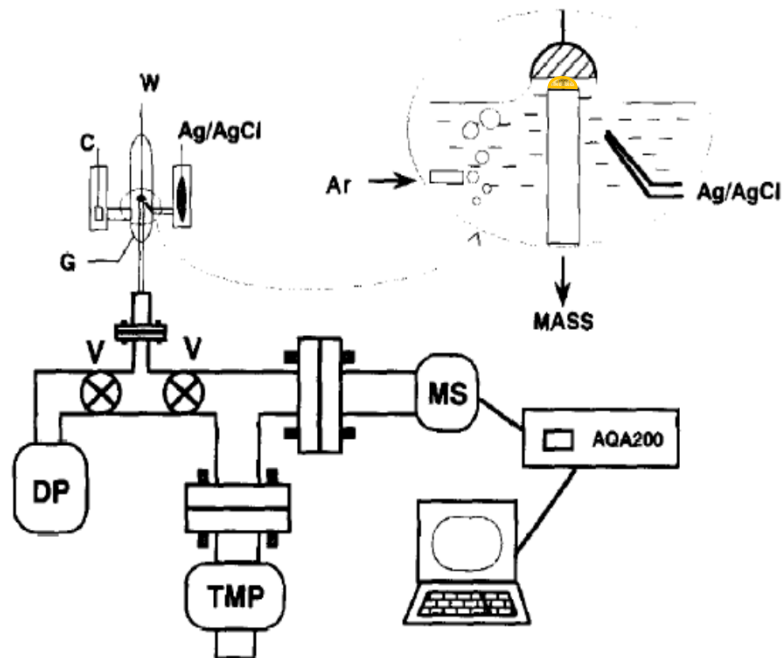


Fig. 1. New on-line mass spectrometer system; MS, mass detector and spectrometer; DP, diffusion pump; TMP, turbomolecular pump; C, counter-electrode; W, working electrode; V, valve; G, gas pipe. The inset shows the gas-inlet system.

pinhole:  $d = \text{few } \mu\text{m}$

Teflon membrane

advantage: hanging meniscus

small amount of substance

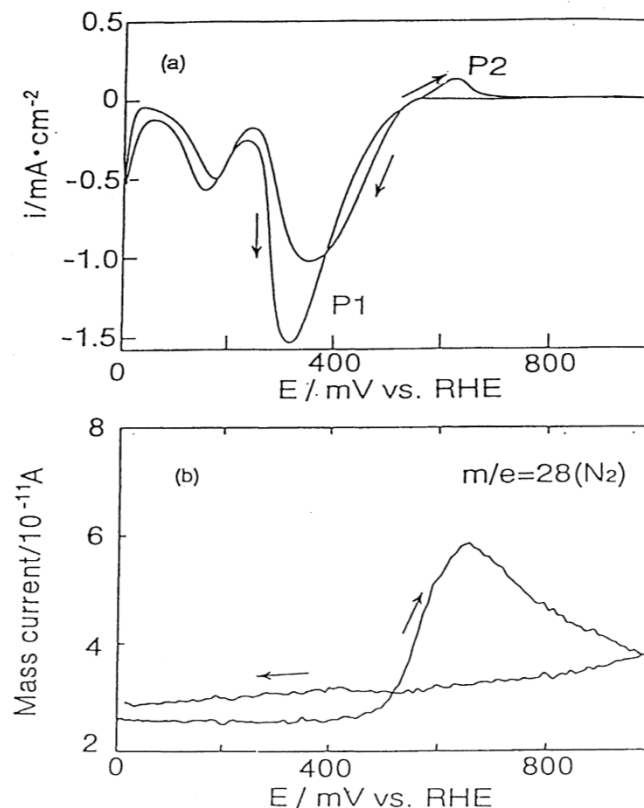


Fig.1. Cyclic voltammogram (a) and corresponding Mass current of  $\text{N}_2$  (b) at Pt(100) in  $0.2\text{M Na}_3\text{PO}_4 + 2\text{ mM NO}_2^-$ . Sweep rate,  $2\text{ mVs}^{-1}$ .

Gao, Y.; Tsuji, H.; Hattori, H.; Kita, H., New on-line mass spectrometer system designed for platinum single crystal electrode and electroreduction of acetylene. *Journal of Electroanalytical Chemistry* **1994**, 372, 195 - 200.

Gao, Y. Z.; Kita, H.; Hattori, H., DEMS STUDY OF  $\text{NO}_2^-$  REDUCTION ON Pt(100) ELECTRODE IN ALKALINE-SOLUTION. *Chemistry Letters* **1994**, (11), 2093-2096



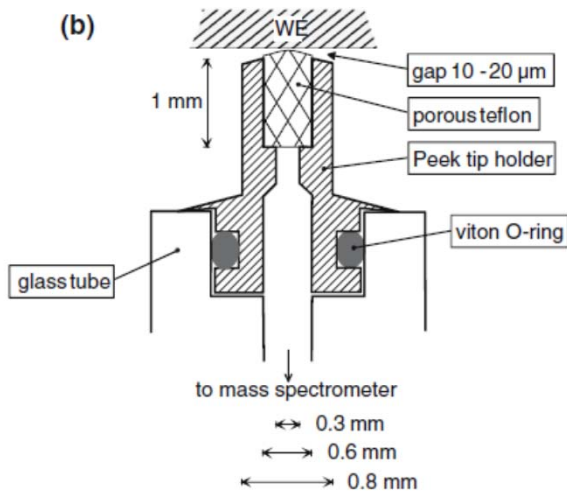
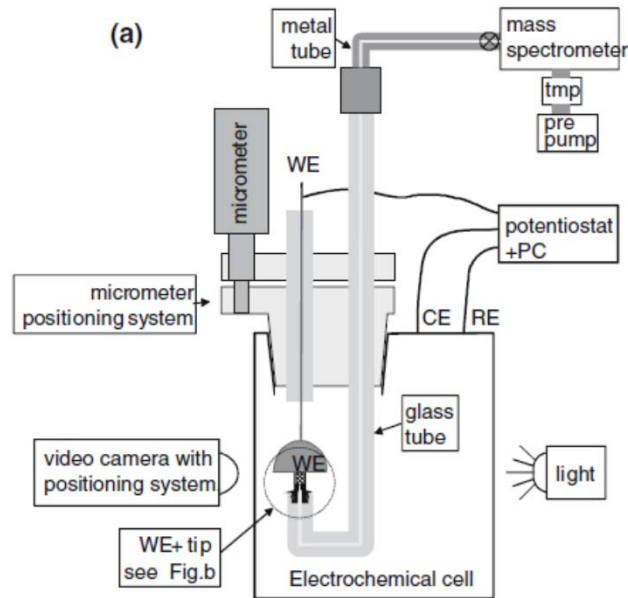


Fig. 1. (a) Schematic drawing of the on-line electrochemical MS setup. WE – Working Electrode, RE – Reference Electrode, CE – Counter Electrode, tmp-turbo molecular pump. (b) Schematic drawing of the on-line electrochemical MS tip.

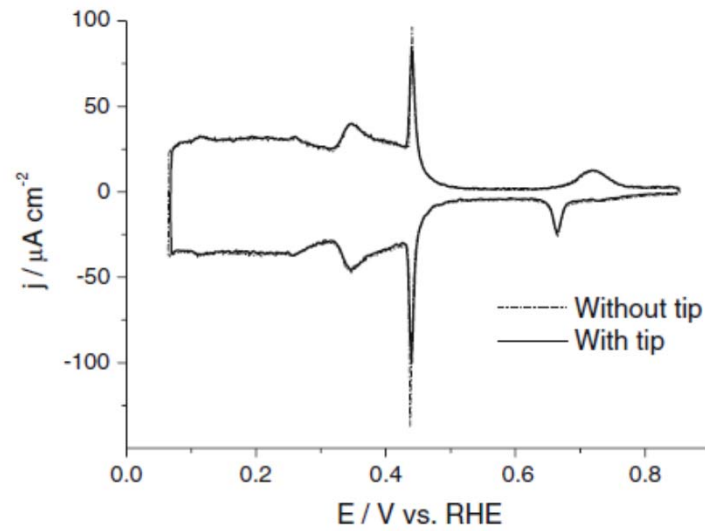
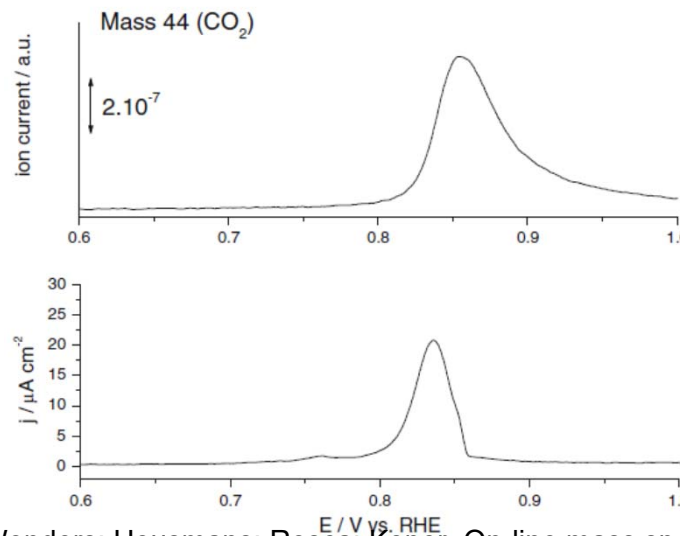
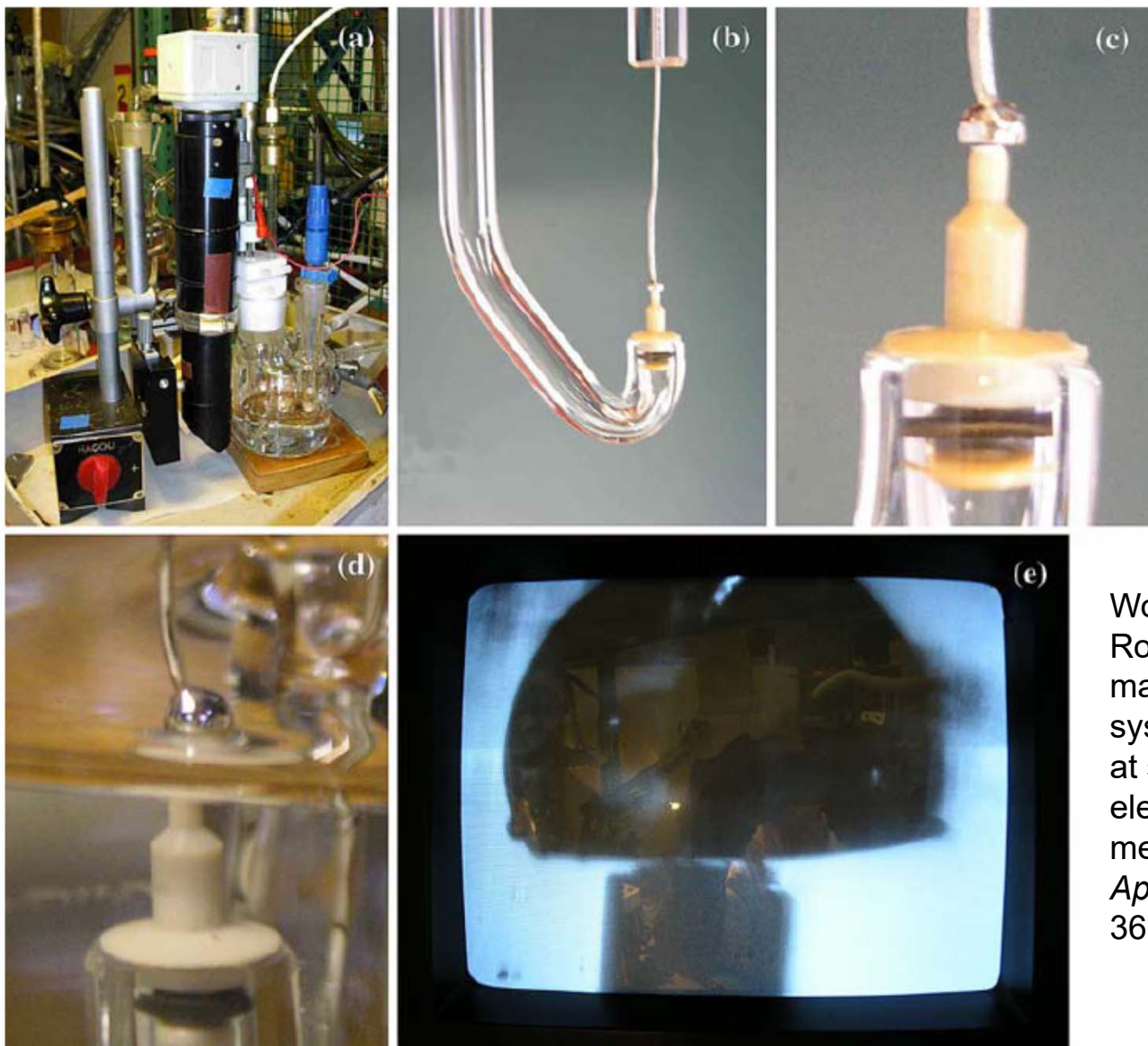


Fig. 3. Blank voltammogram of a Pt(111) electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 50 mV/s, with the on-line electrochemical MS tip retracted and with the tip in close proximity (10–20 μm) to the electrode.



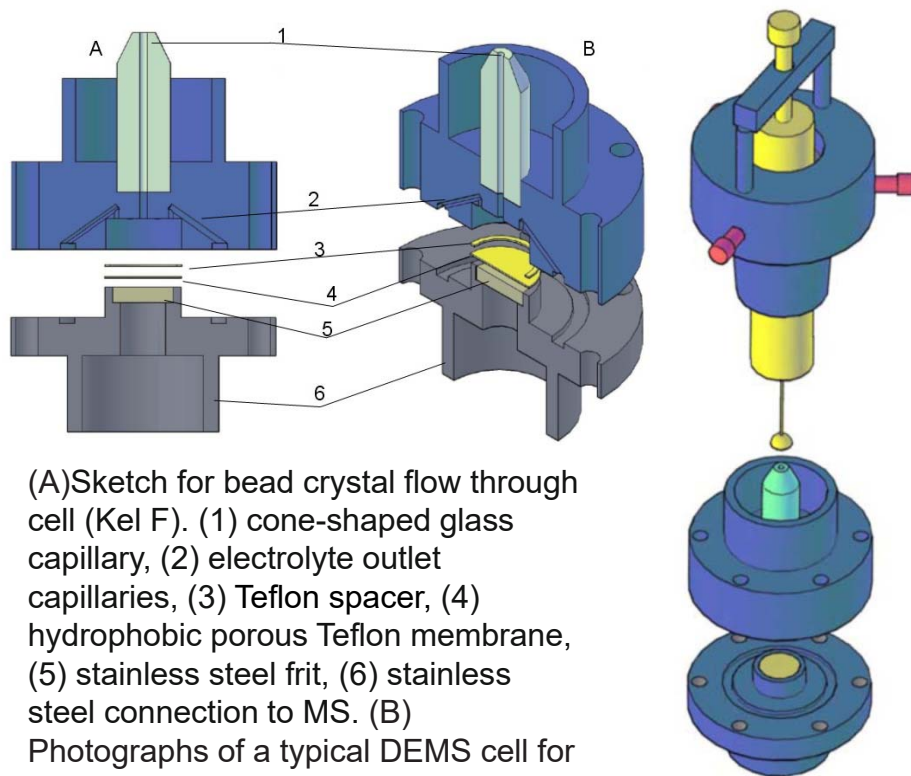
CO stripping voltammogram and associated mass signal for CO<sub>2</sub> for a Pt(111) electrode at 2 mV s<sup>-1</sup>.

Wonders; Housmans; Rosca; Koper, On-line mass spectrometry system for measurements at single-crystal electrodes in hanging meniscus configuration. *J. Appl. Electrochem.* **2006.** 36. (11). 1215

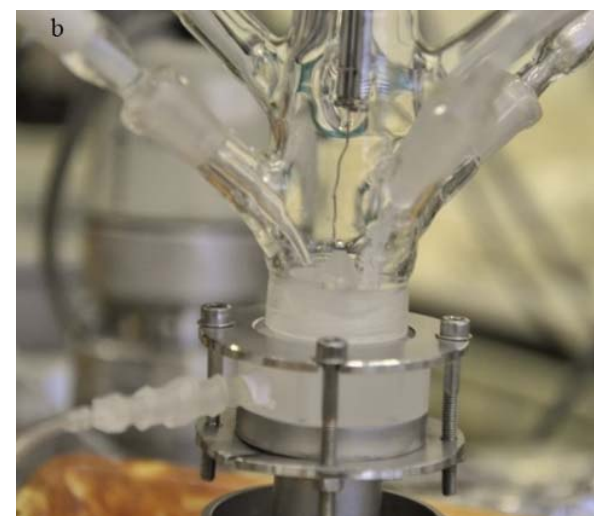


Wonders; Housmans; Rosca; Koper, On-line mass spectrometry system for measurements at single-crystal electrodes in hanging meniscus configuration. *J. Appl. Electrochem.* **2006**, 36, (11), 1215

Fig. 2. Photographs of (a) electrochemical cell with the tip configuration and connection to the MS. (b) and (c) Tip – bead-type electrode configuration, (d) tip-electrode in hanging meniscus, (e) view of the tip-electrode configuration on the video screen.



(A) Sketch for bead crystal flow through cell (Kel F). (1) cone-shaped glass capillary, (2) electrolyte outlet capillaries, (3) Teflon spacer, (4) hydrophobic porous Teflon membrane, (5) stainless steel frit, (6) stainless steel connection to MS. (B) Photographs of a typical DEMS cell for bead crystals. (A coloured electrolyte was used for better visibility).



**Advantage:**

- bead single crystals (2-3 mm).
- Hanging meniscus configuration.
- Defined convection.

Abd-El-Latif, A. A.; Xu, J.; Bogolowski, N.; Königshoven, P.; Baltruschat, H., New Cell for DEMS Applicable to Different Electrode Sizes. *Electrocatalysis* **2012**, 3, (1), 9.

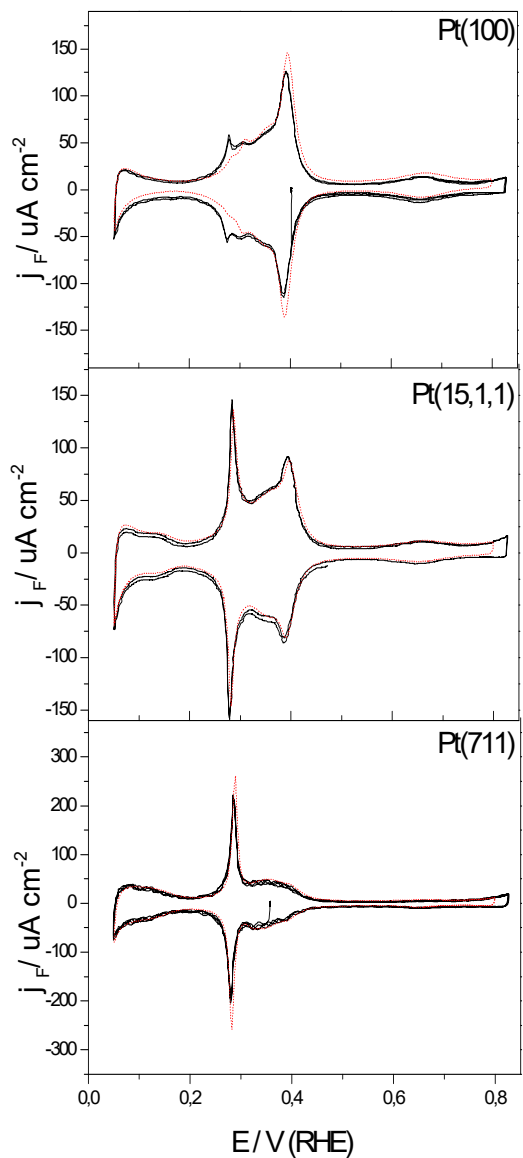


Fig.4. Voltammetric profiles of Pt(100), Pt(15,1,1) and Pt(711) electrodes in 0.1 M H<sub>2</sub>SO<sub>4</sub>,  $v = 50$  mV/s, in DEMS cell(solid line) and in standard H-type cell(dotted line).

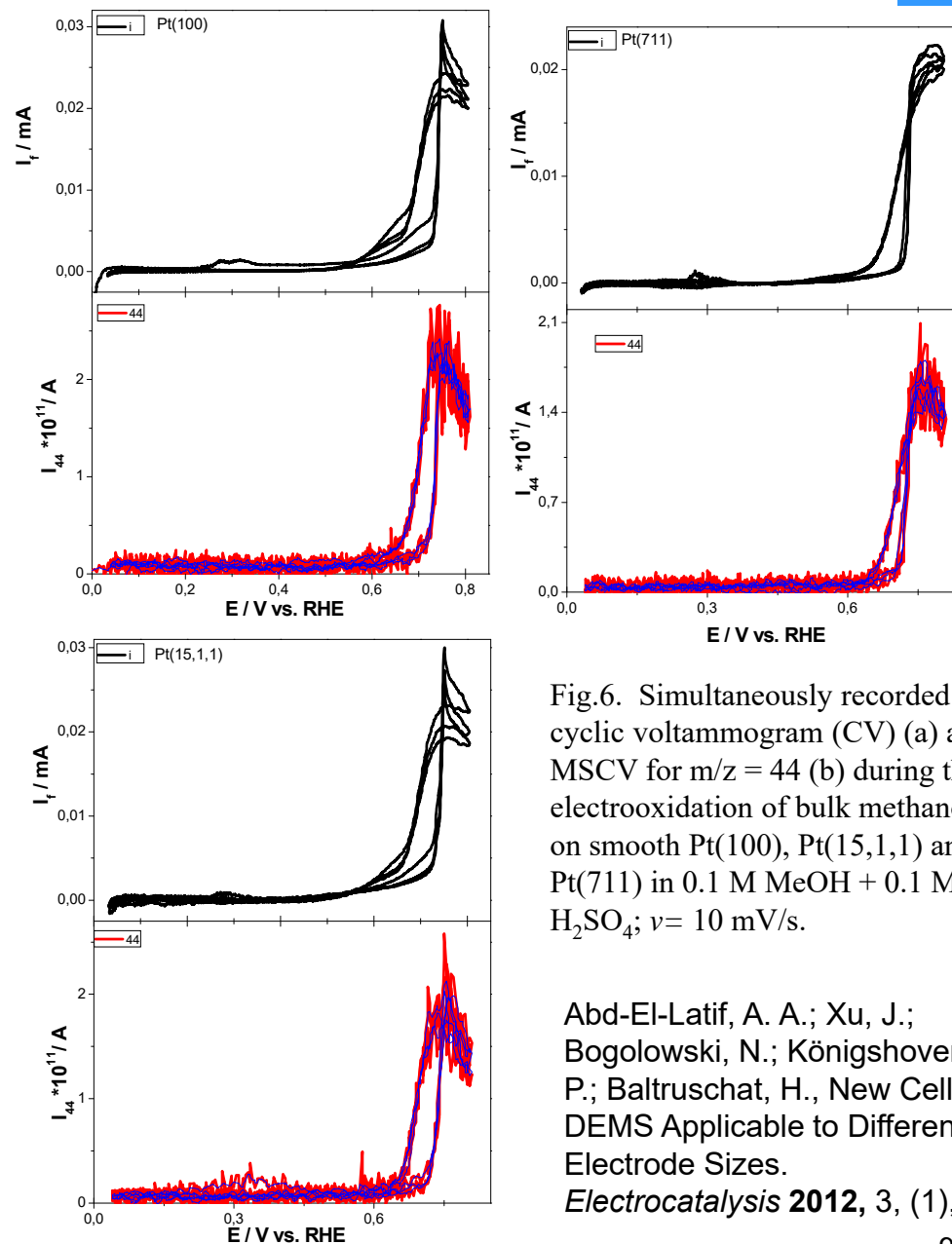


Fig.6. Simultaneously recorded cyclic voltammogram (CV) (a) and MSCV for  $m/z = 44$  (b) during the electrooxidation of bulk methanol on smooth Pt(100), Pt(15,1,1) and Pt(711) in 0.1 M MeOH + 0.1 M H<sub>2</sub>SO<sub>4</sub>;  $v = 10$  mV/s.

Abd-El-Latif, A. A.; Xu, J.; Bogolowski, N.; Königshoven, P.; Baltruschat, H., New Cell for DEMS Applicable to Different Electrode Sizes. *Electrocatalysis* **2012**, 3, (1), 9

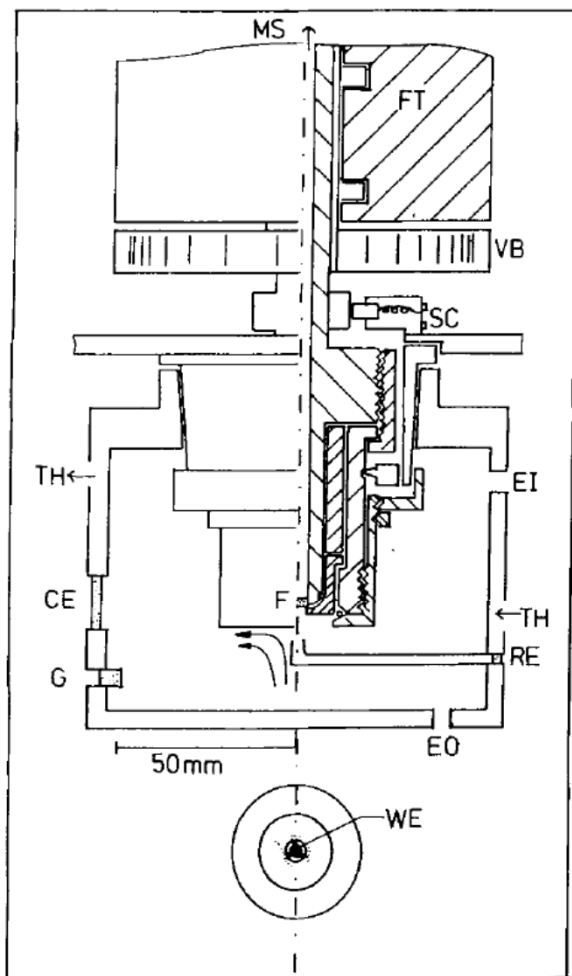


Fig. 2

Rotating inlet system and electrochemical cell; MS = mass spectrometer, FT = rotating feed through, VB = V-belt drive, SC = sliding contact, EI = electrolyte inlet, FH = in- and outlet for thermostat, RE = reference electrode, WE = working electrode (front view below, contact wire dotted), CE = counter electrode, G = gas inlet, F = metal frit, EO = electrolyte outlet

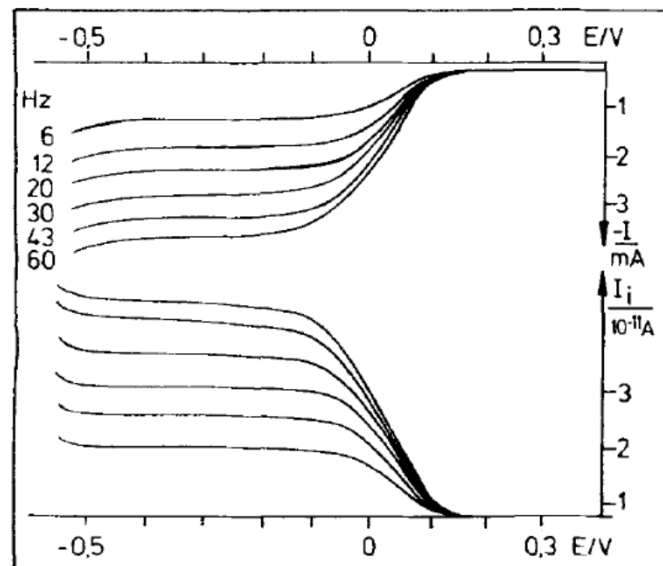


Fig. 5

Diffusion limiting current for H<sub>2</sub> evolution on the sputtered Pt-electrode (above) and simultaneously measured mass intensity curves of H<sub>2</sub> (below); electrolyte: 10<sup>-3</sup> m HClO<sub>4</sub> + 0.1 m NaClO<sub>4</sub>; sweep rate 7 mVs<sup>-1</sup>; rotation speeds in Hz as indicated

Tegtmeyer, D.; Heindricks, A.; Heitbaum, J., Electrochemical on line mass spectrometry on a rotating electrode inlet system. *Berichte der Bunsengesellschaft für Physikalische Chemie* **1989**, 93, 201-206.

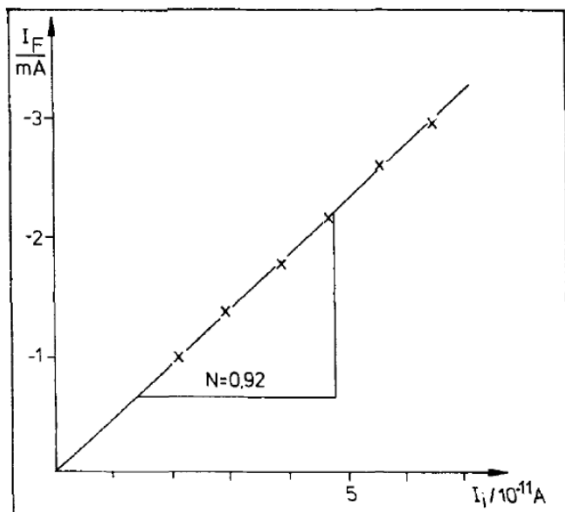


Fig. 6  
 $I_F$  vs.  $I_i$  diagram for curves shown in Fig. 5;  $N$  is determined from slope with  $K_{H_2}^0 = 4.9 \cdot 10^{-3}$  As/mol

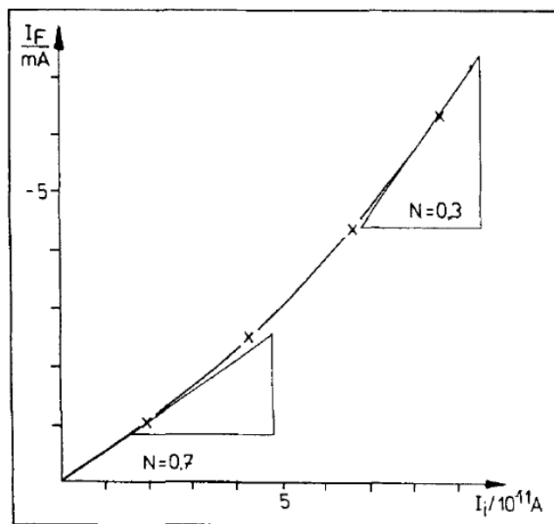


Fig. 7  
 $I_F$  vs.  $I_i$  diagram for  $H_2$ -evolution on the lacquer electrode;  $N$  is determined from the slopes with  $K_{H_2}^0 = 5.5 \cdot 10^{-3}$  As/mol

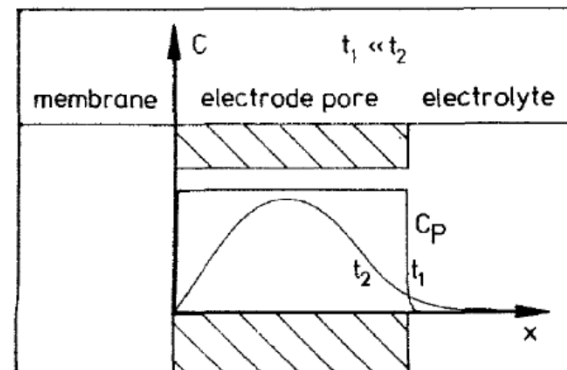


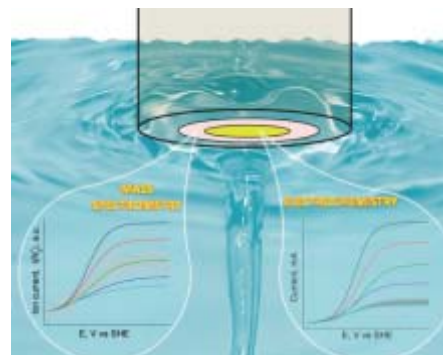
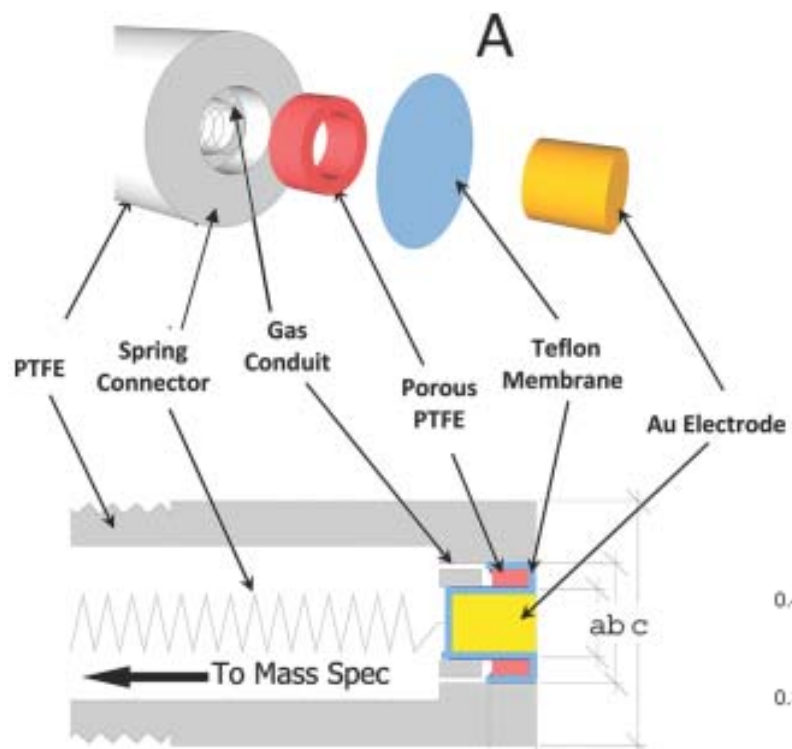
Fig. 10  
 Concentration profiles inside a pore in case of desorption of an adsorbate at two different times  $t_1 \ll t_2$

Table 1  
 Collection efficiencies for  $CO_2$  formation out of adsorbed  $CO$  on the sputtered and the lacquer Pt-electrode at different rotation speeds

Rotation speed (Hz)	0	4	10	16	25	30
$N$ (sputtered electrode)	0.92	0.89	0.88	0.89	0.9	0.88
$N$ (lacquer electrode)	0.62	0.52	0.54	0.51	0.54	0.52

Tegtmeyer, D.; Heindrichs, A.; Heitbaum, J., Electrochemical on line mass spectrometry on a rotating electrode inlet system. *Berichte der Bunsengesellschaft für Physikalische Chemie* **1989**, 93, 201-206.

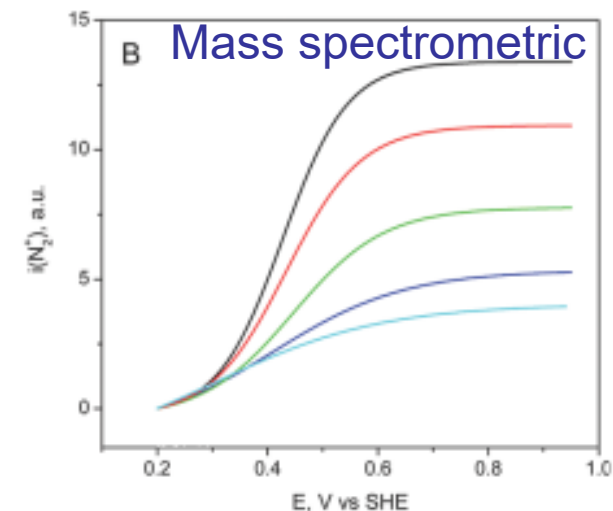
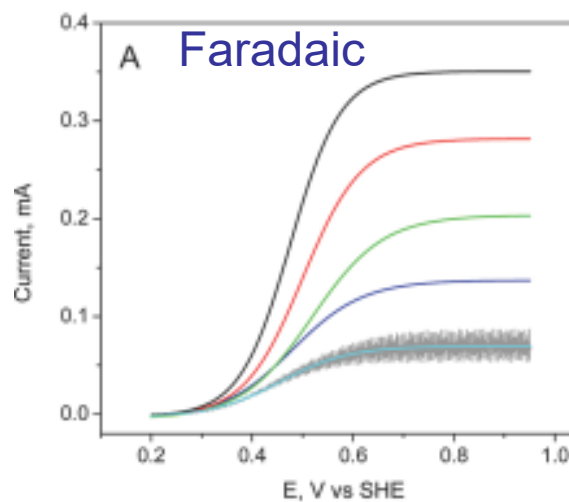
# Membrane ring / Au disk: Wall-jet DEMS



I. Treufeld *et al.*, *Anal. Chem.* 84 (2012) 5175 – 5179

$\text{N}_2\text{H}_4$  oxidation to  $\text{N}_2$

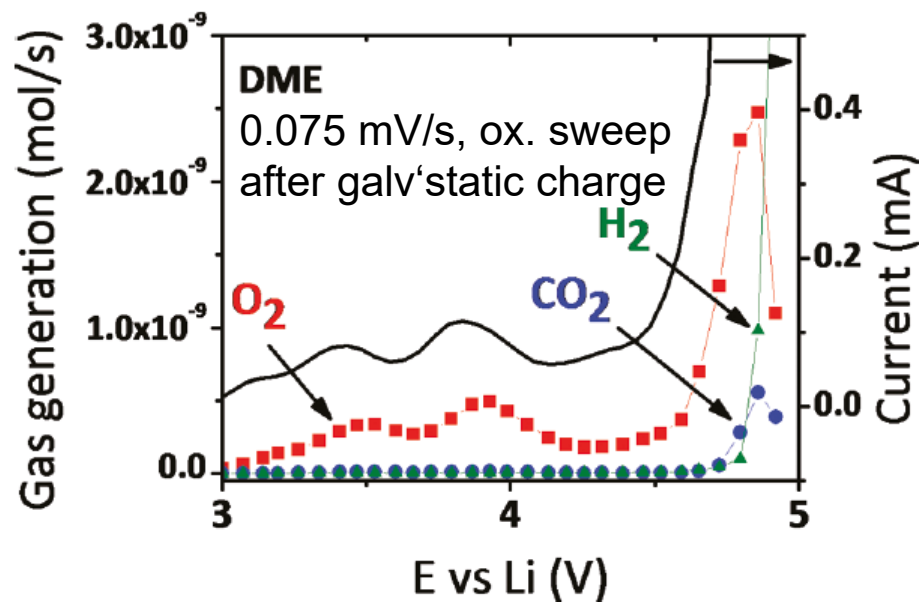
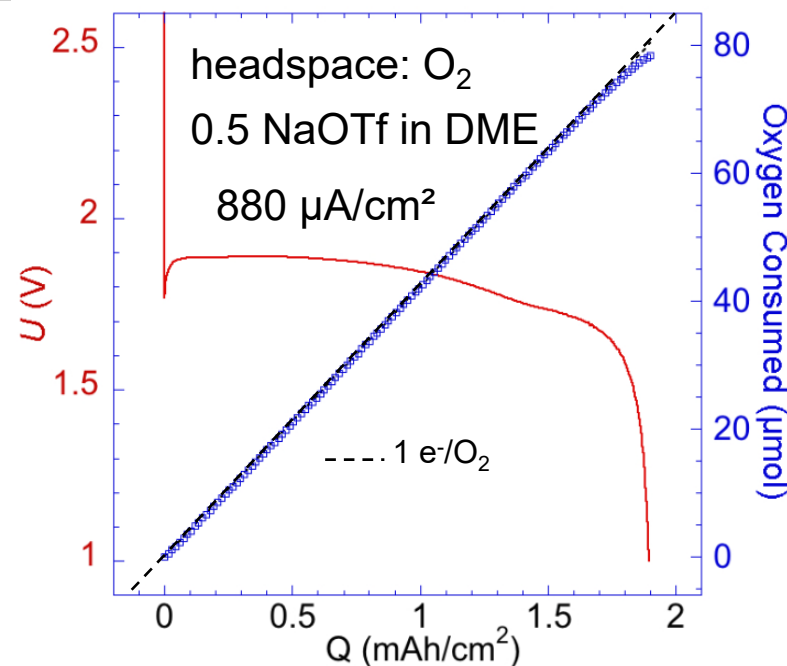
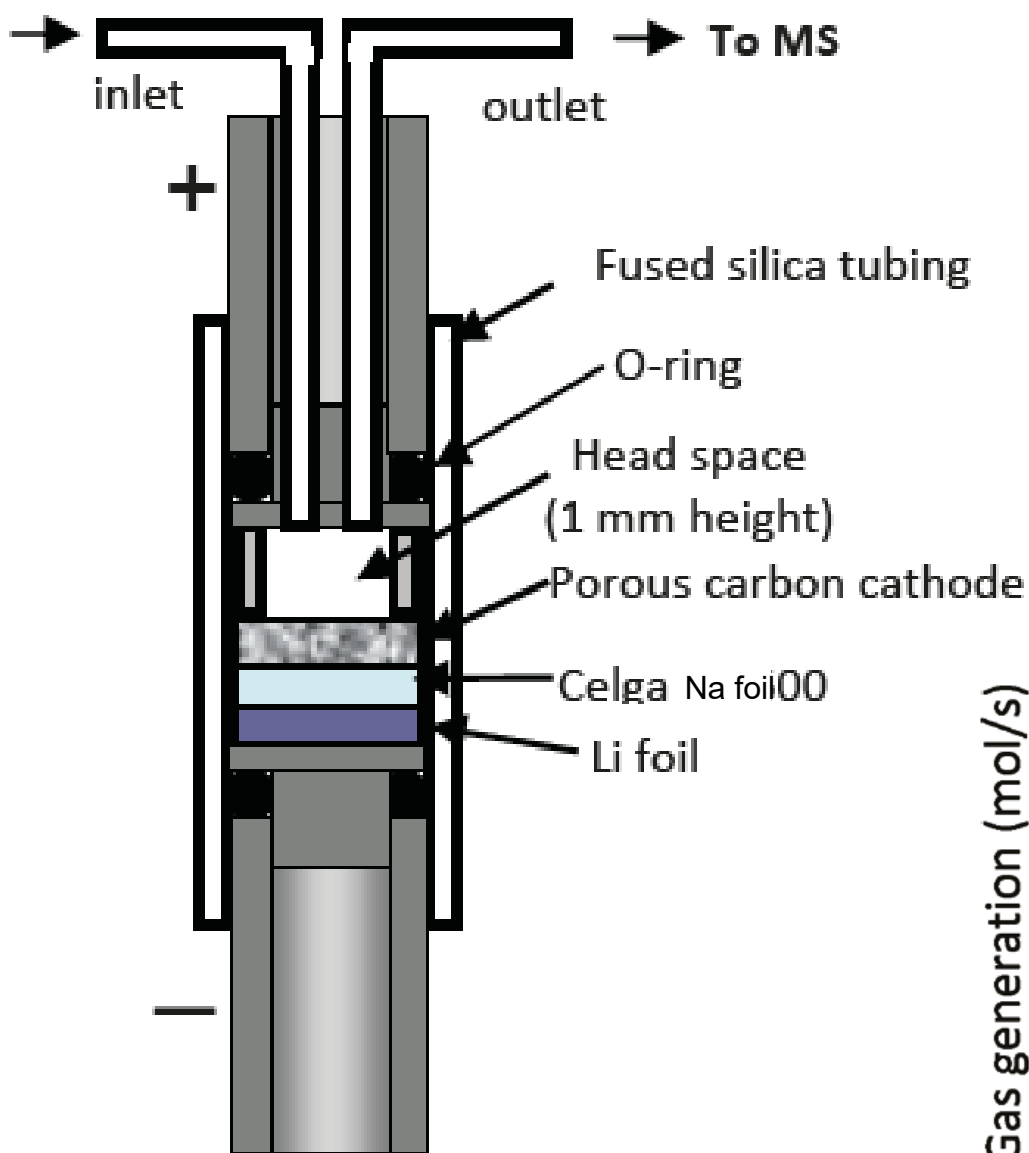
- Hydrodynamic cell
- Fast time response
- Complicated design



Combination with devices  
(batteries and fuel cells)



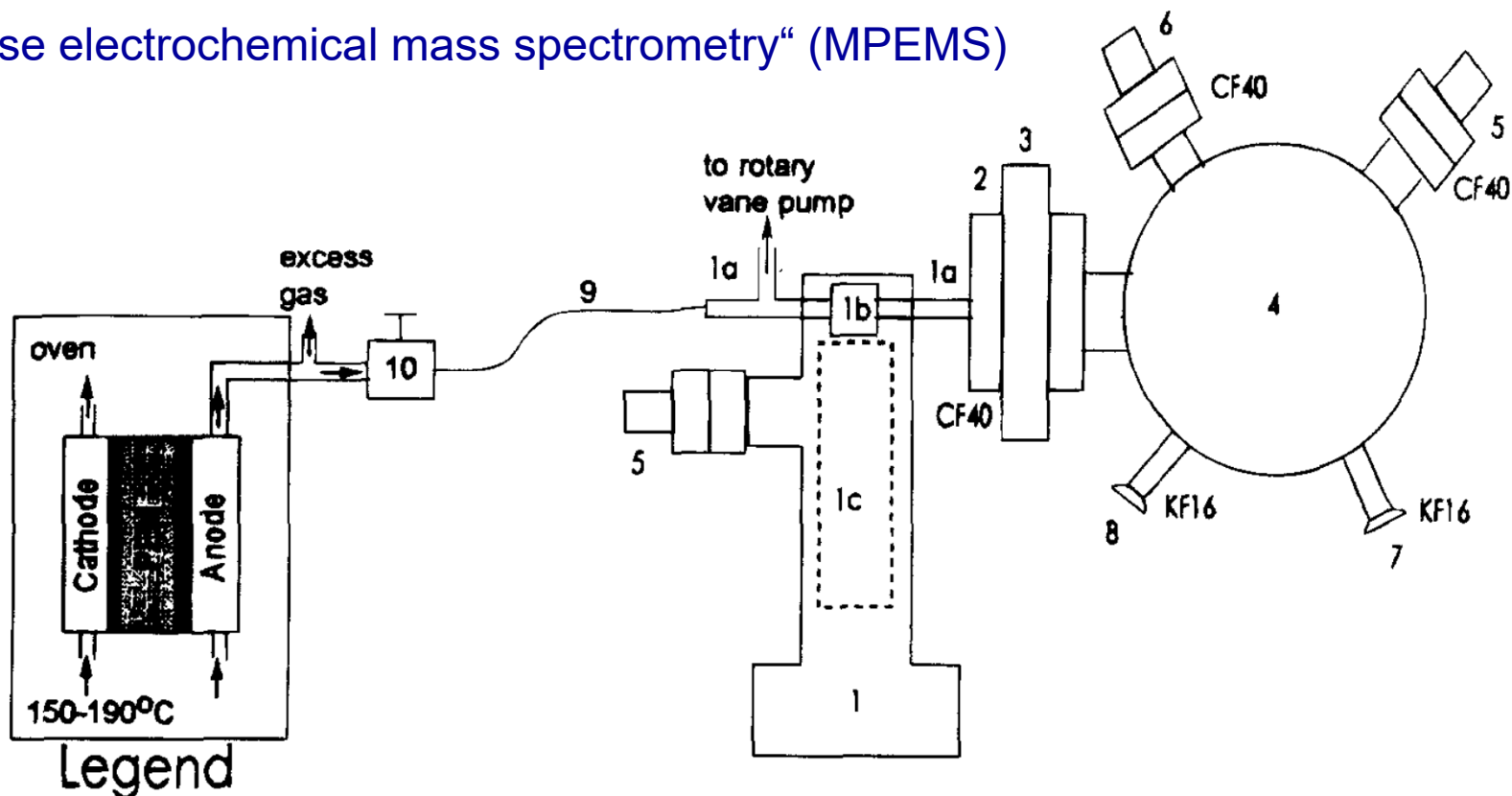
# Cell types



(1) McCloskey, B. D.; Bethune, D. S.; Shelby, R. M.; Girishkumar, G.; Luntz, A. C. *J. Phys. Chem. Lett.* **2011**, *2*, 1161-1166.

(2) Nichols, J. E.; McCloskey, B. D. *J. Phys. Chem. C* **2016**, *121*, 85-96.

## „multipurpose electrochemical mass spectrometry“ (MPEMS)



### Legend

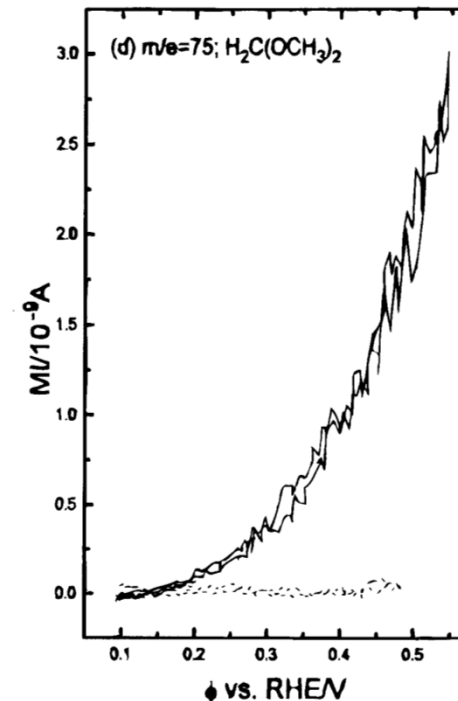
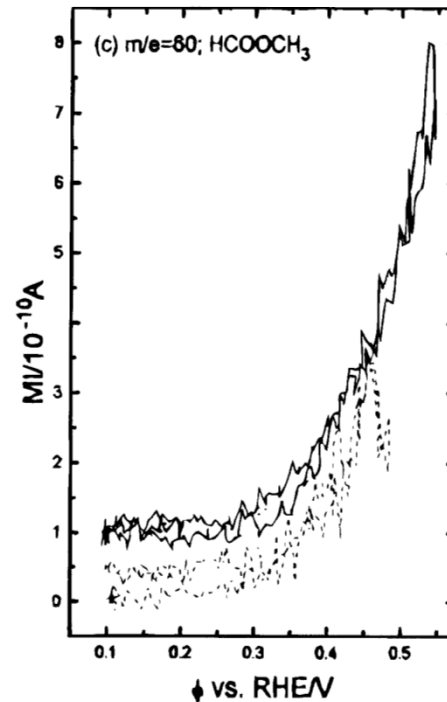
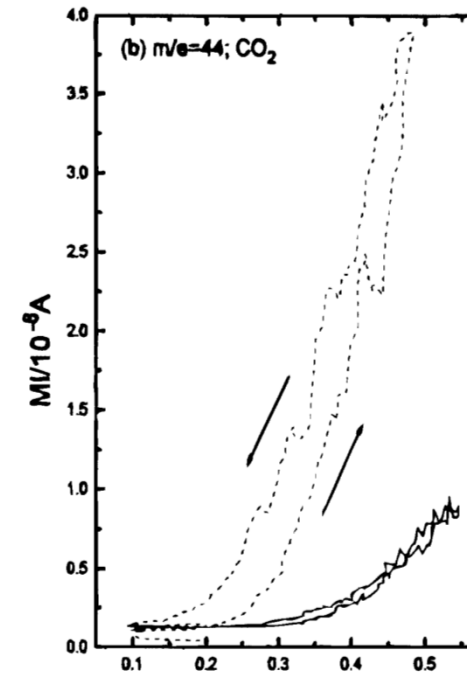
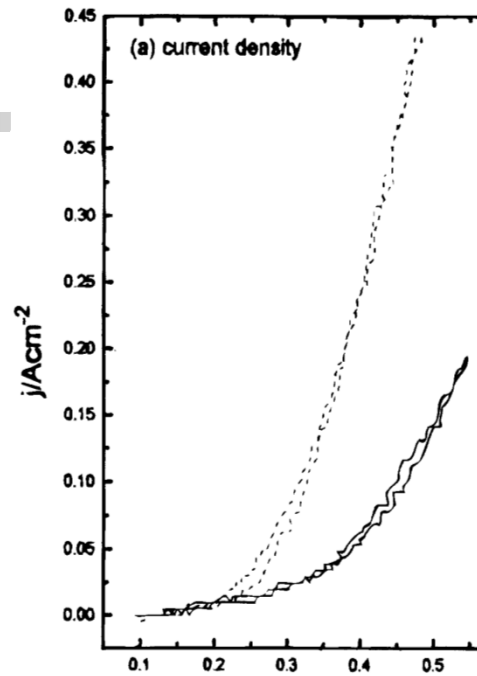
- |                                    |  |
|------------------------------------|--|
| 1 Sensorlab 200D mass spectrometer | 6 vent valve                                   |
| 1a 2 inlets for item 1b            | 7 inlet valve for DEMS                         |
| 1b enclosed ion source             | 8 spare inlet for DEMS; blank flanged          |
| 1c quadrupole system               | 9 Heated capillary for attachment to fuel cell |
| 2 Adapter CF40-1/4" tube           | 10 Valve                                       |
| 3 Gate valve                       |  |
| 4 Custom built vacuum recipient    |  |
| 5 2 x cold cathode tubes           |  |

Schematic diagram of the MPEMS setup including the connection to the DMFC.

# Cell types

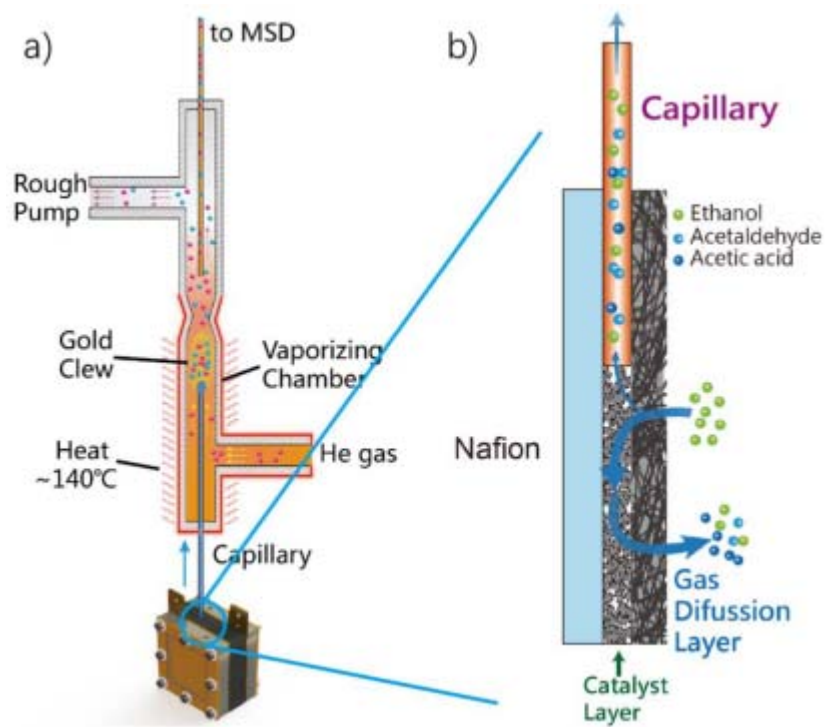


Current density (a) and mass signals (b-d) vs. potential during a potentiodynamic experiment using a prototype DMFC. 1 mV/s. 175~ Electrolyte: PBI membrane doped with 500 m/o H3PO4. Anode: platinum-ruthenium, 4 mg/cm2, feed rate adjusted by vacuum system of the MS (2 to 3 liquid ml/h). Cathode: platinum black, 4 mg/cm2, 10 ml/min air. Solid curves; pure methanol feed. Dashed curves; water/methanol mole ratio: 2.



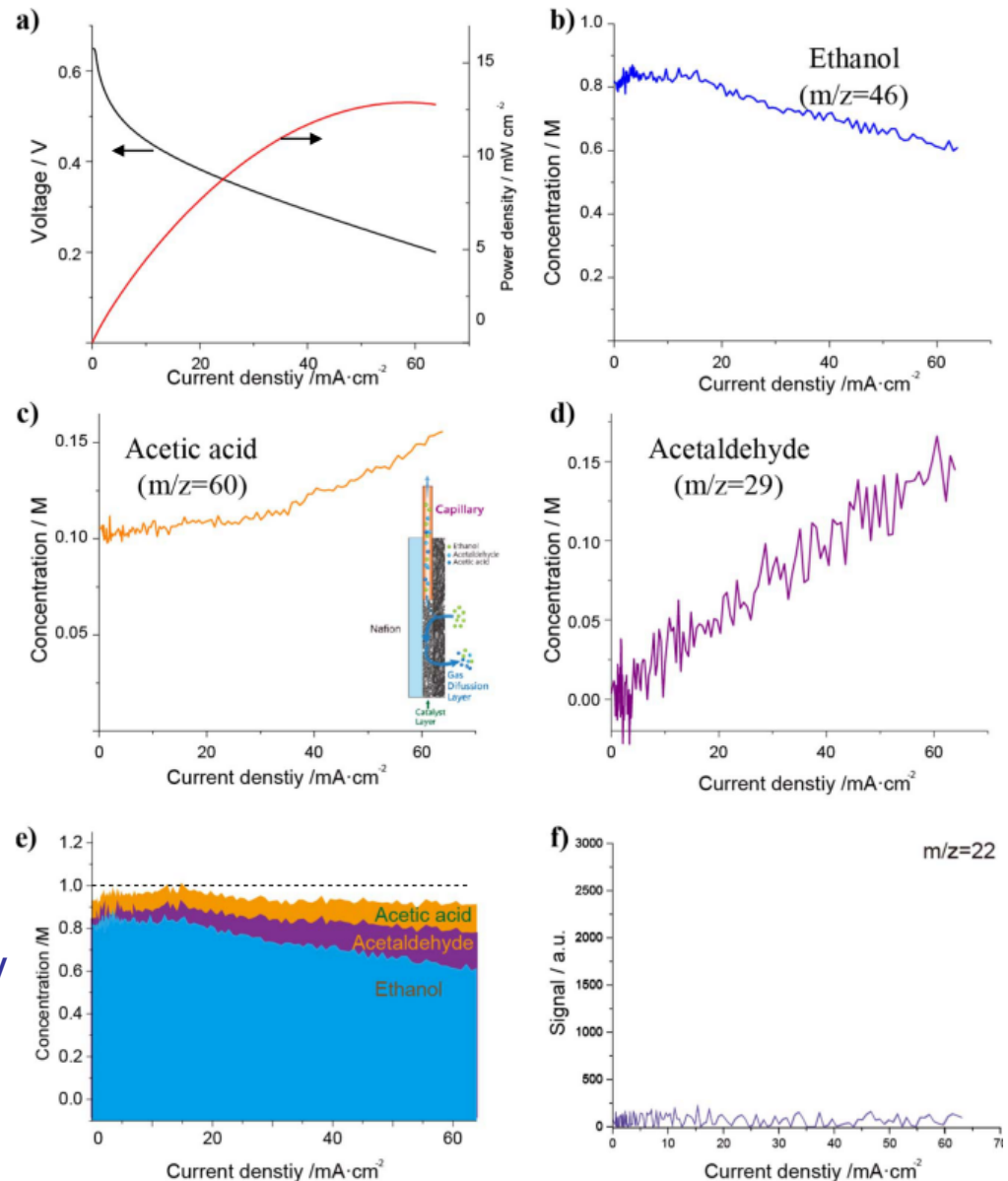
S. Wasmus, J.-T. Wang, and R. F. Savinell, *J. Electrochem. Soc.*, Vol. 142, 1995, 3825

# Liquid inlet OLEMS: *in operando* monitoring of direct ethanol fuel cells



Y.-H. Hong *et al.*, *Electrochem. Comm.* 87 (2018) 91

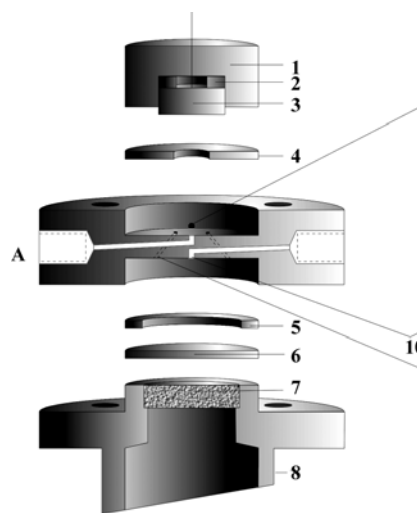
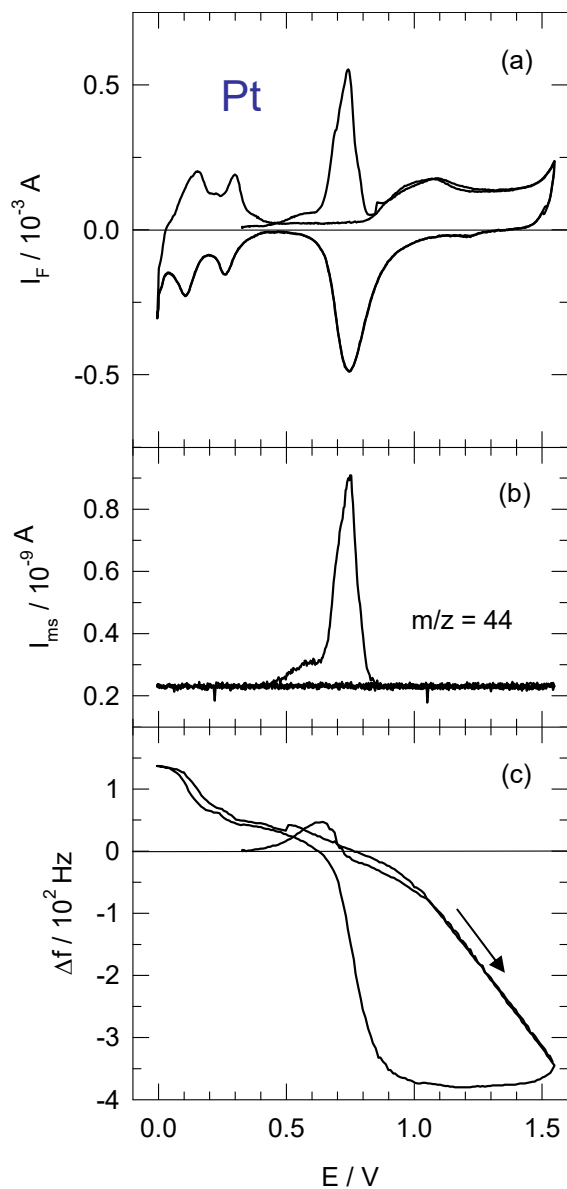
- liquid-inlet OEMS via sampling capillary
- liquid sampling and vaporization
- detection of low-volatility species



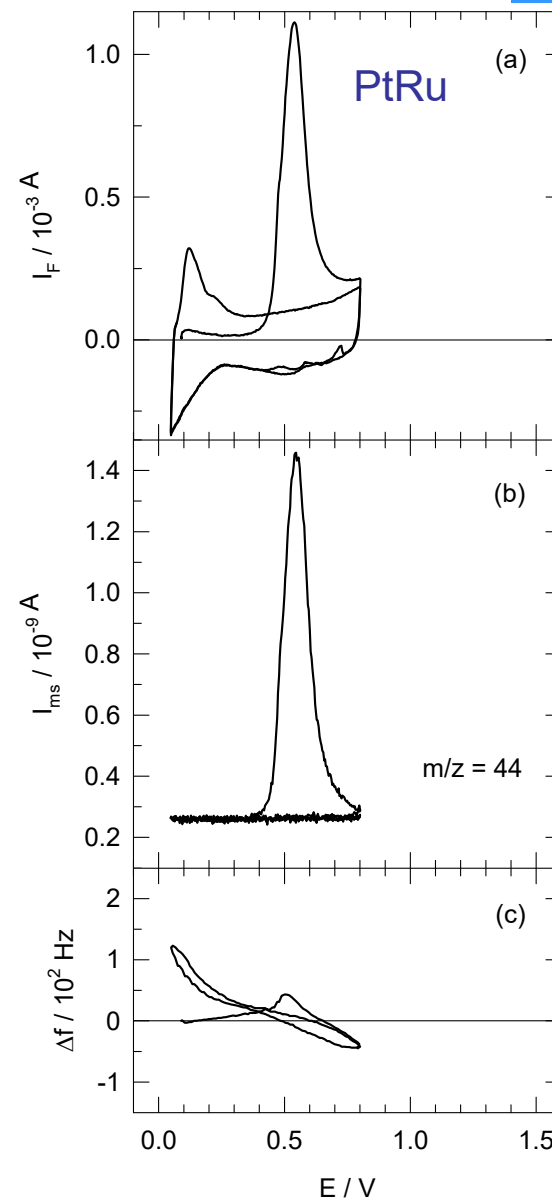


## Combination of DEMS with other methods

# DEMS dual thin layer flow cell: EQCM combined with DEMS

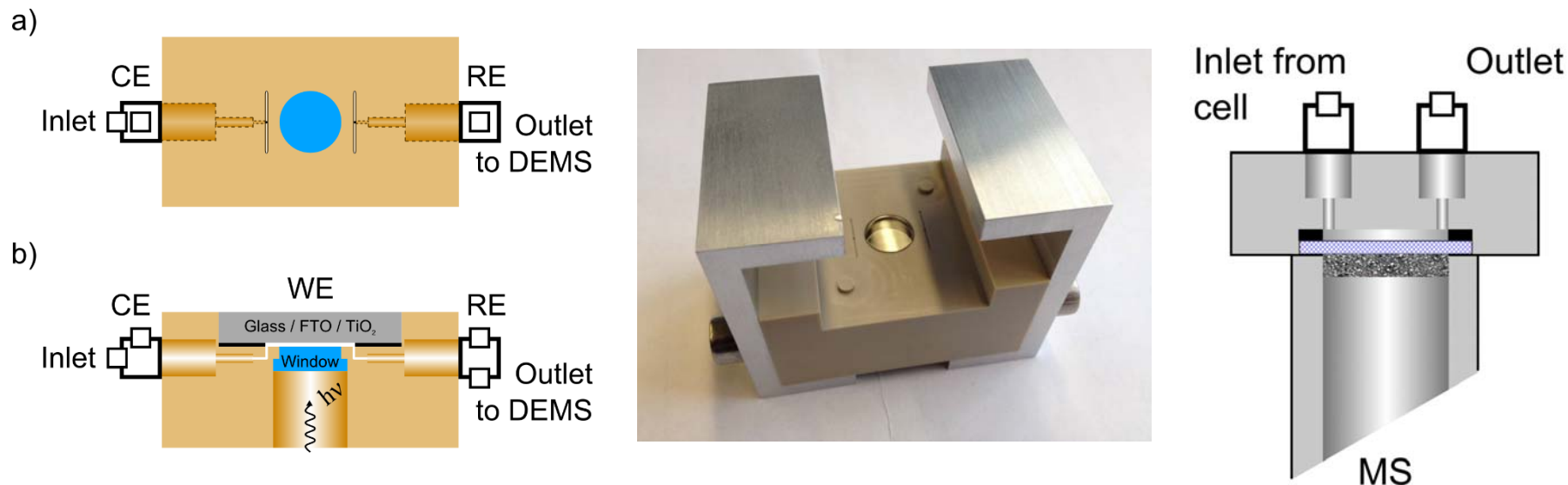


- In single measurement: Faradaic, mass spectrometric currents and frequency change
- Frequency (mass) change:
  - COad desorption (oxidation)
  - MeOx formation
  - anion adsorption/ desorption



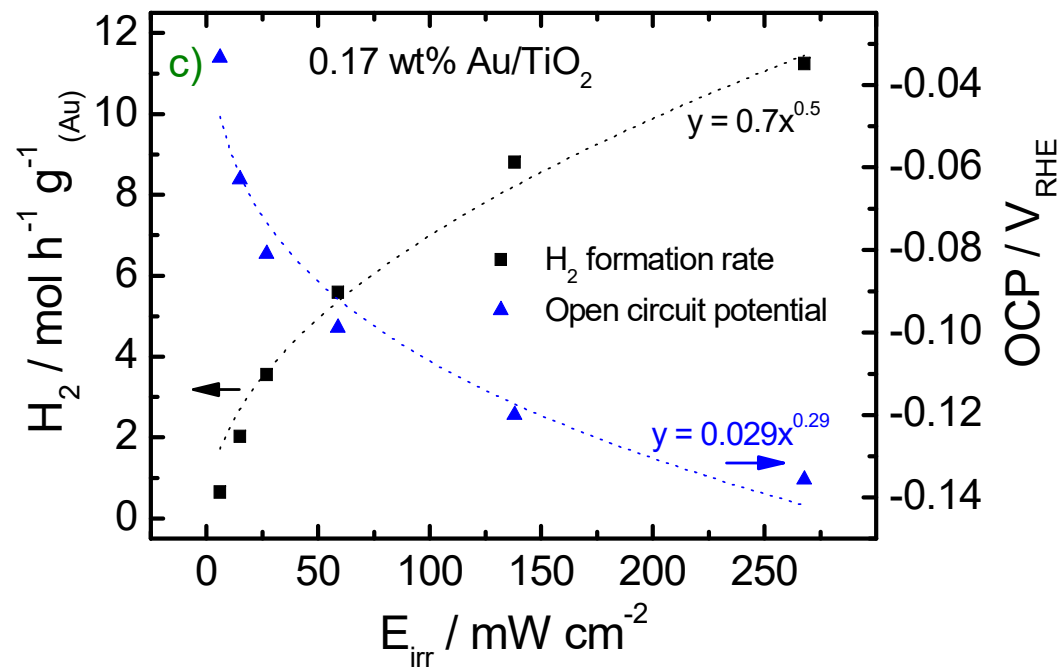
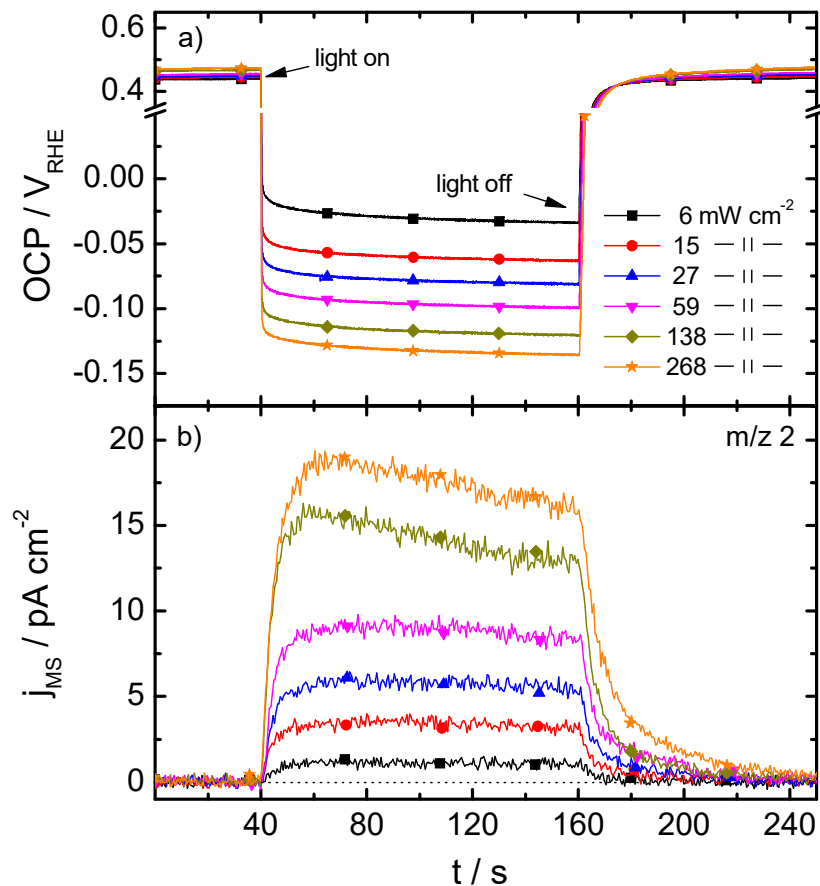
Z. Jusys et al., J ECS 146 (1999) 1093

# Photo-DEMS flow cell: light-induced $H_2$ formation on $Au/TiO_2$



- Circular photo-electrode fabricated over FTO coated glass
- The glass slice pressed against the tightener (electrode down)
- The outlet from the photo flow cell connected to membrane inlet unit
- The photo electrode illuminated via quartz window by Hg(Xe) lamp
- Water filter used between the lamp and the cell to absorb the heat

# Photo-DEMS flow cell: light-induced H<sub>2</sub> formation on Au/TiO<sub>2</sub>

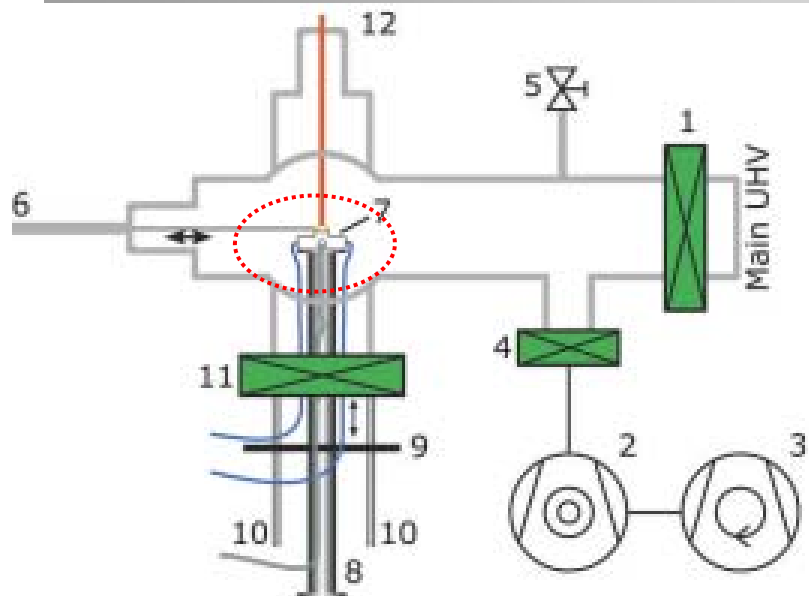


R. Reichert *et al.*,  
 PCCP 16 (2014) 25076  
 JPCC 119 (2015) 24750

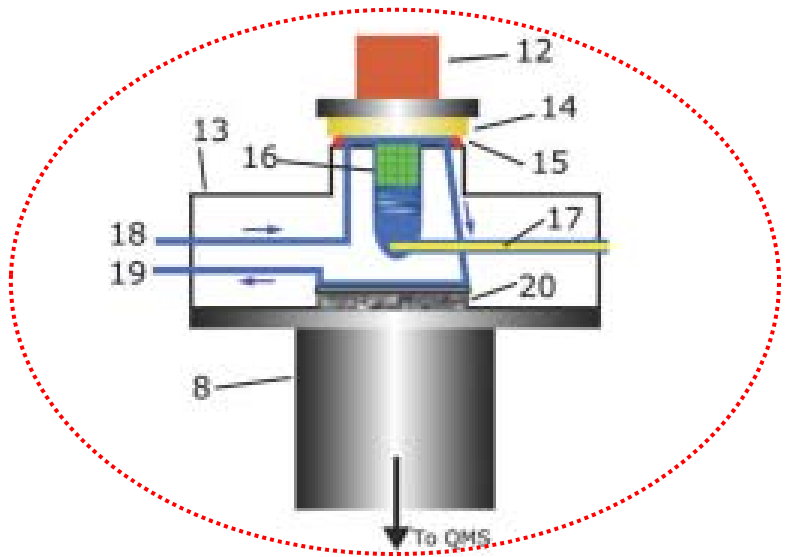
- Photo-electrochemical DEMS measurements
- Photo-catalytic H<sub>2</sub> formation measured online
- OCP and H<sub>2</sub> formation dependence on light intensity



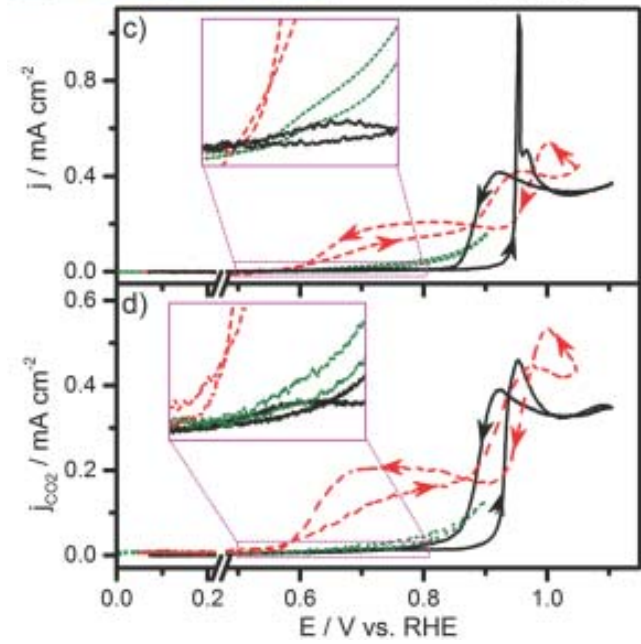
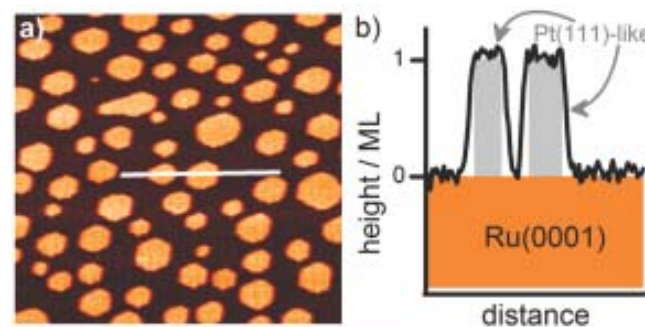
# UHV-STM prepared/ characterized electrodes: DEMS flow cell



DEMS flow cell coupled to UHV

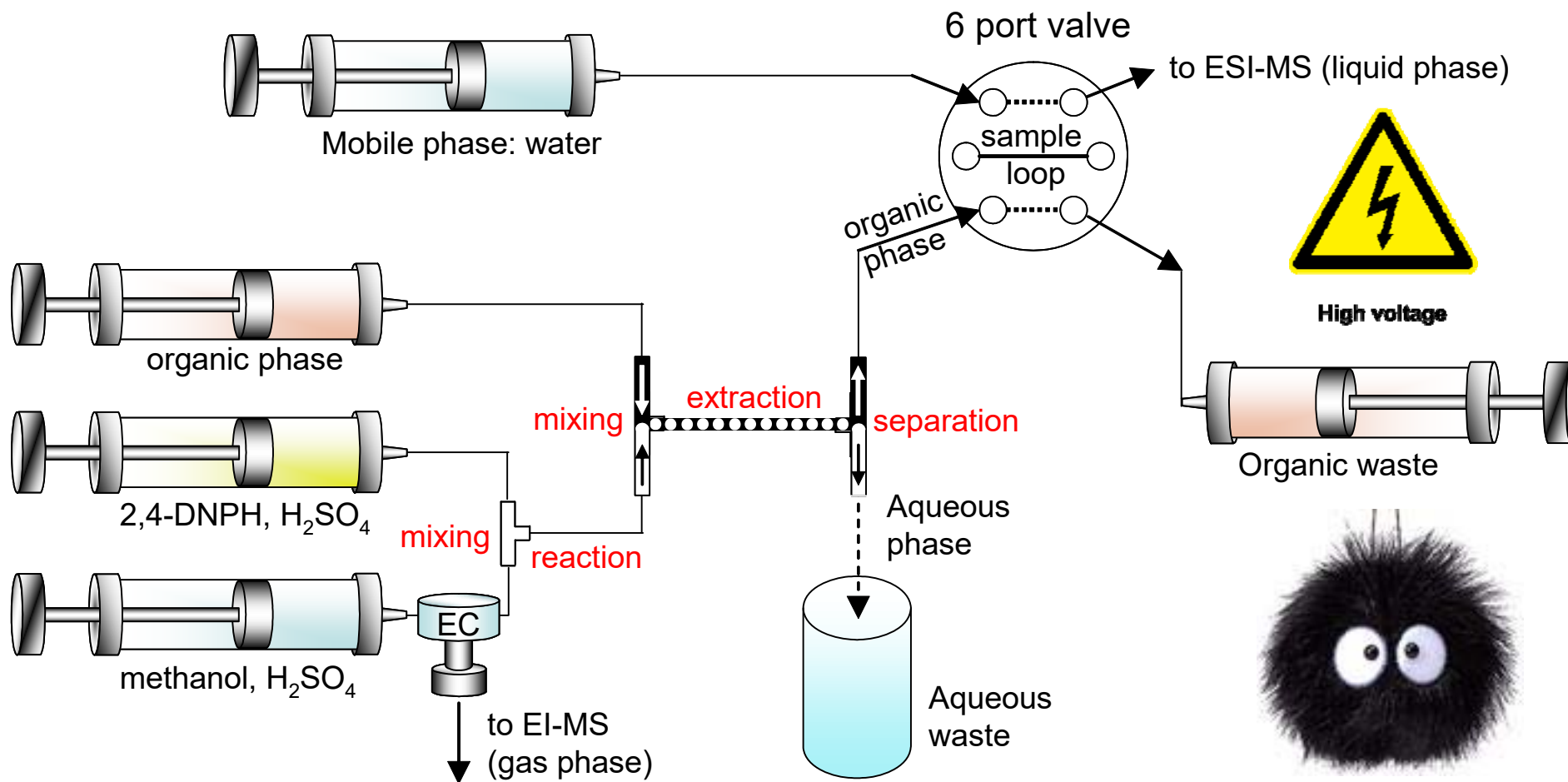


J. Schnaidt *et al.*, PCCP 19 (2017) 4166



- UHV preparation / characterization
- DEMS under controlled mass transport
- Back-transfer to UHV / characterization

# Online detection of both gaseous and non-volatile products



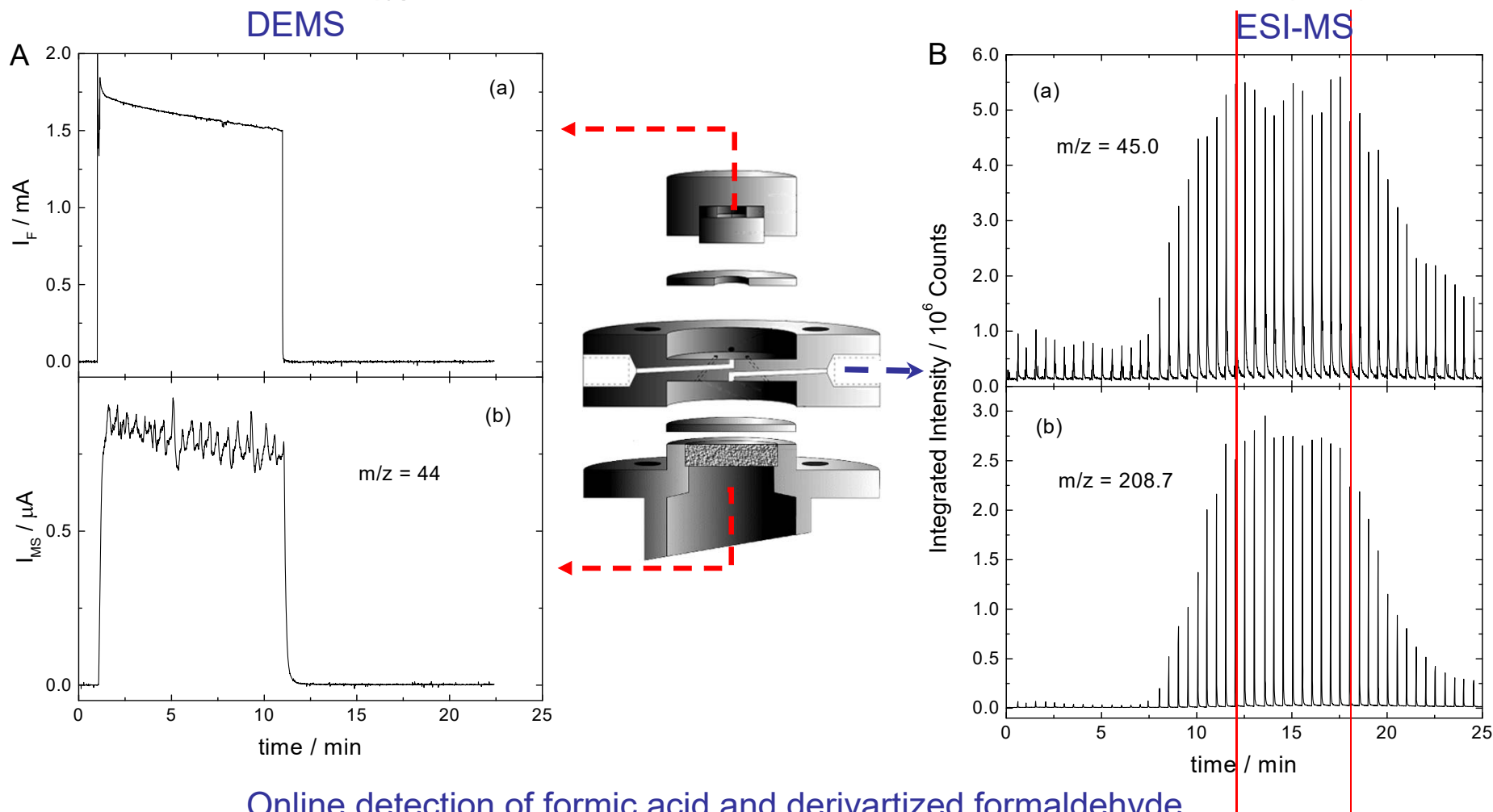
- Decouple syringe pump, potentiostat and DEMS from ESI-MS (-5 kV) via isolation transformer

W. Zhao *et al.*, *Anal. Chem.* 84 (2012) 5479

# Combined DEMS/ESI-MS: potential-step methanol oxidation



Pt / Vulcan:  $28 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ , flow rate:  $0.05 \text{ ml min}^{-1}$ , potential step:  $0.1 \rightarrow 0.65 \rightarrow 0.1 \text{ V (RHE)}$

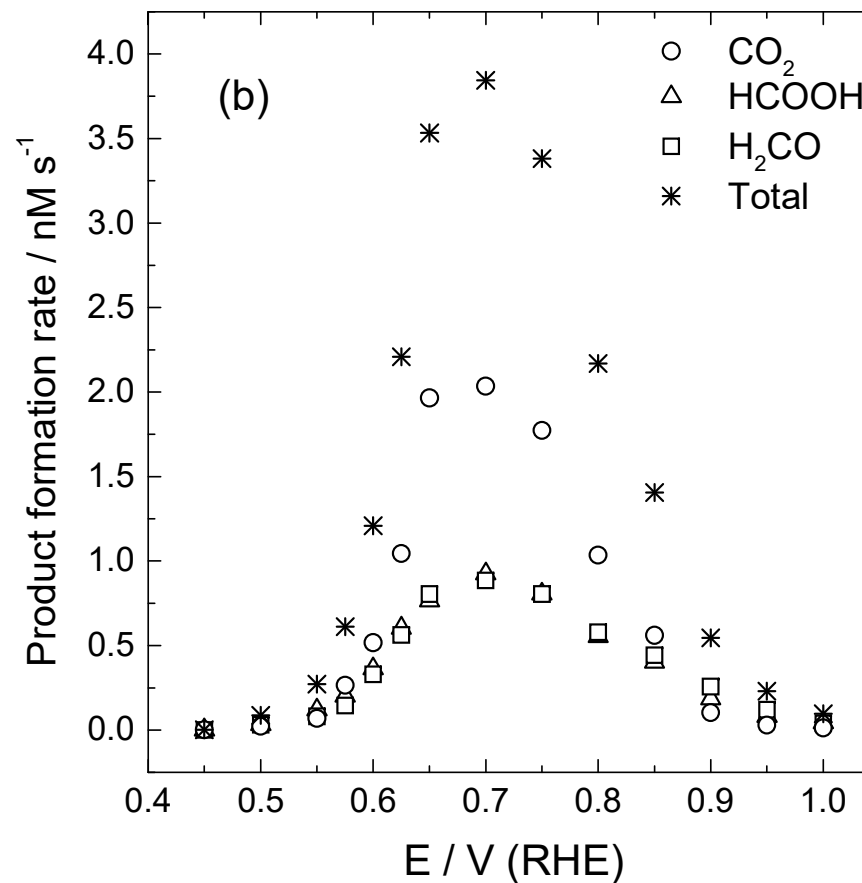
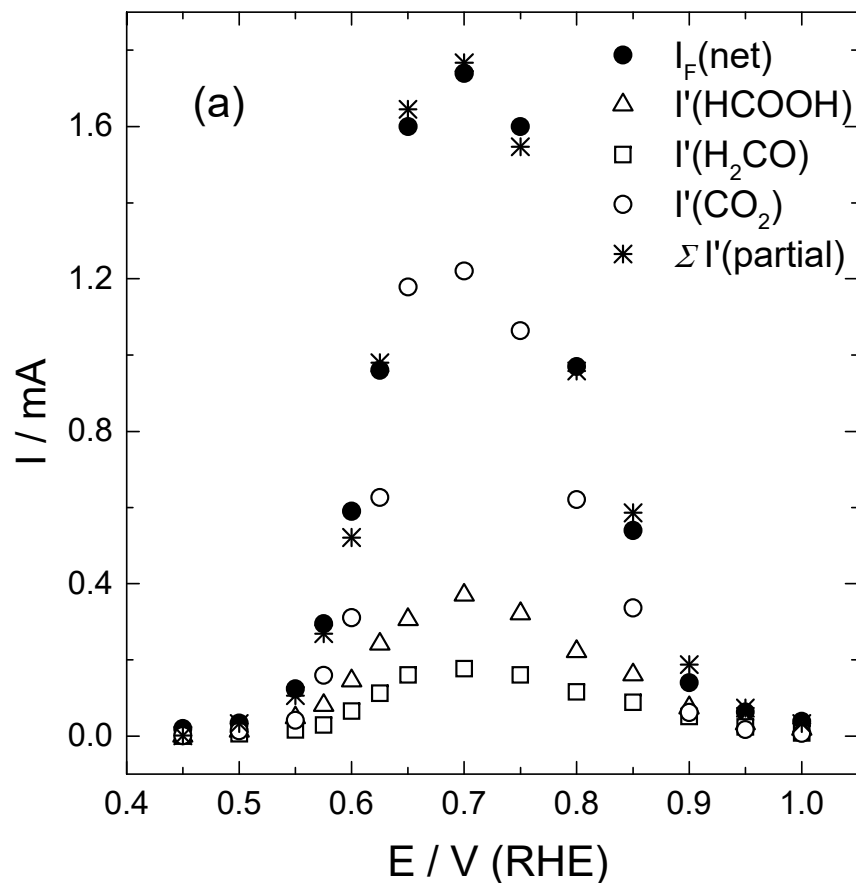


Online detection of formic acid and derivartized formaldehyde

➤ significant time delay between DEMS and ESI-MS signals

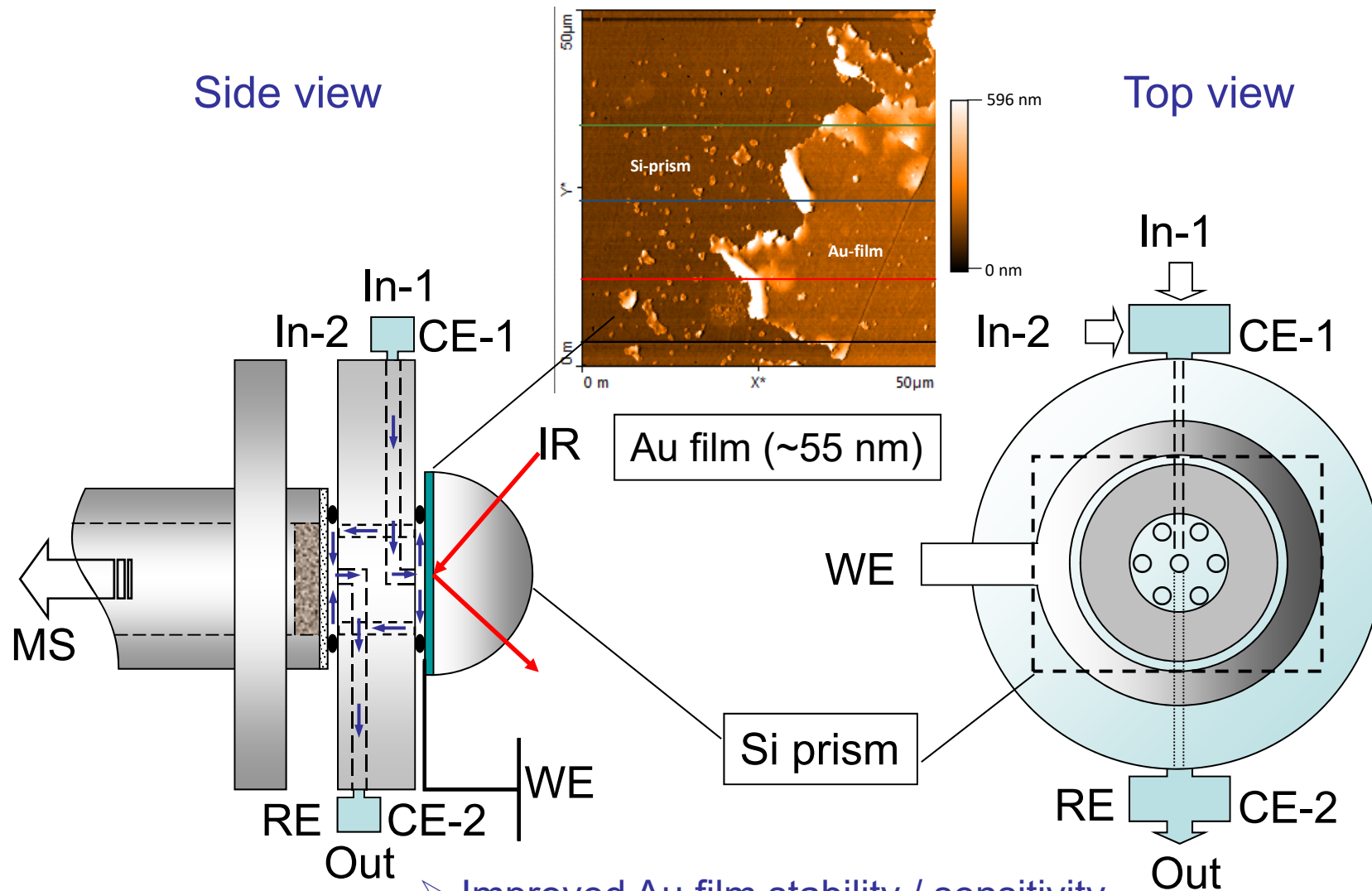
W. Zhao *et al.*, *Anal. Chem.* 84 (2012) 5479

# Combined DEMS/ESI-MS: complete analysis of MOR products



- Both volatile and non-volatile methanol oxidation products quantified
- Combined DEMS/ESI-MS can be used for other complex reactions

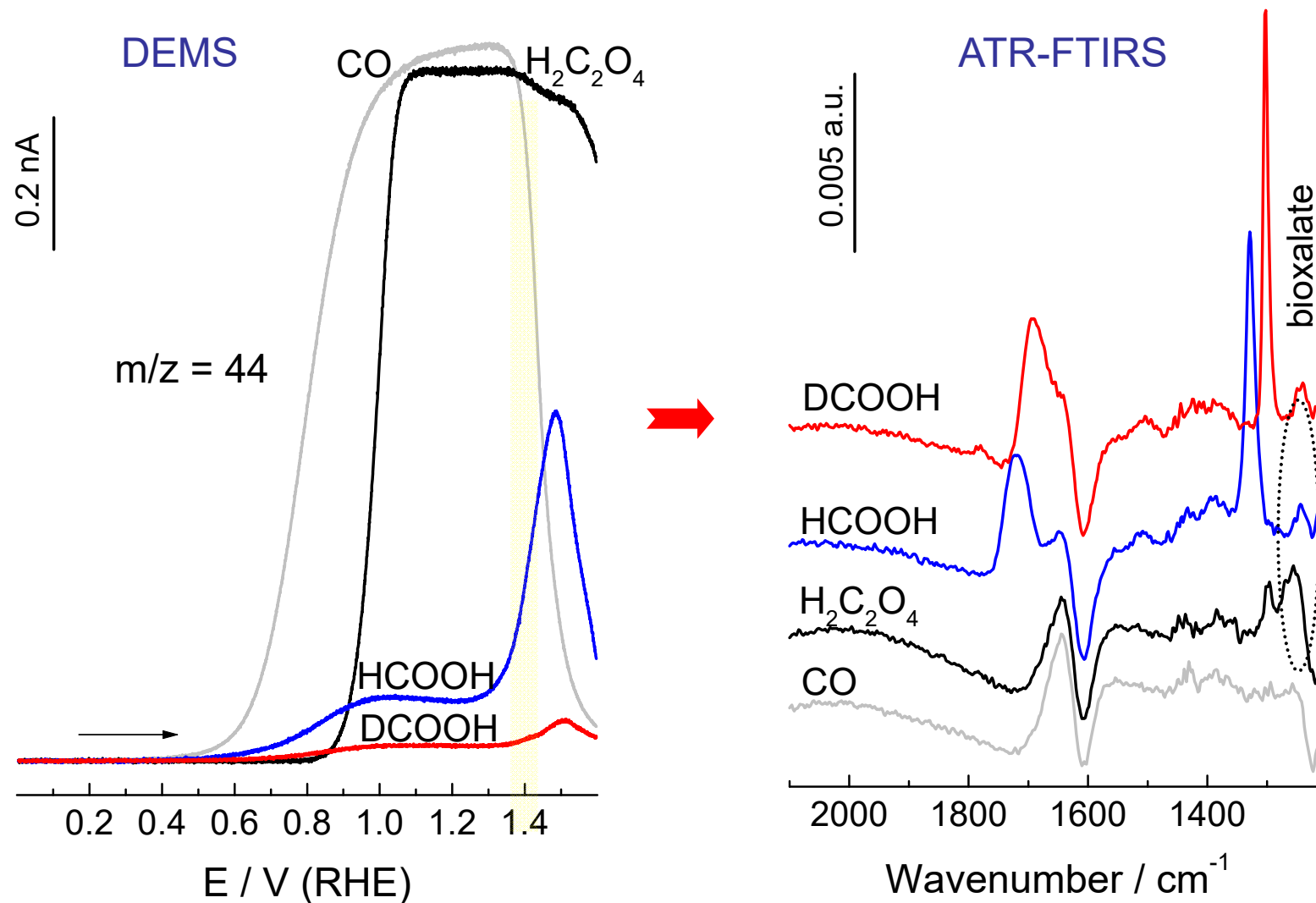
# Combined DEMS / ATR-FTIRS setup



- Improved Au film stability / sensitivity
- Continuous mass transport in a flow cell

M. Heinen *et al.* EA 52 (2007) 5634; Z. Jusys *et al.*, JEAC 800 (2017) 60

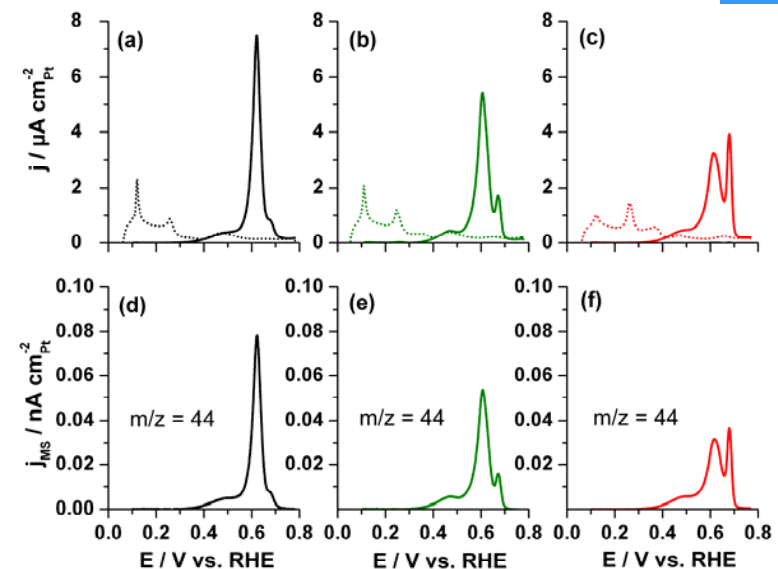
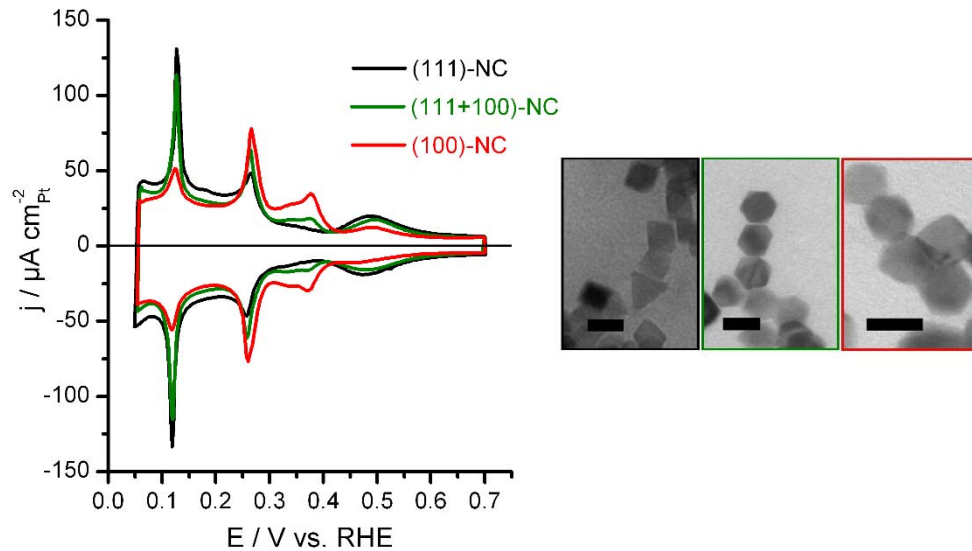
# DEMS / ATR-FTRS: CO, oxalic acid, and formic acid oxidation on Au



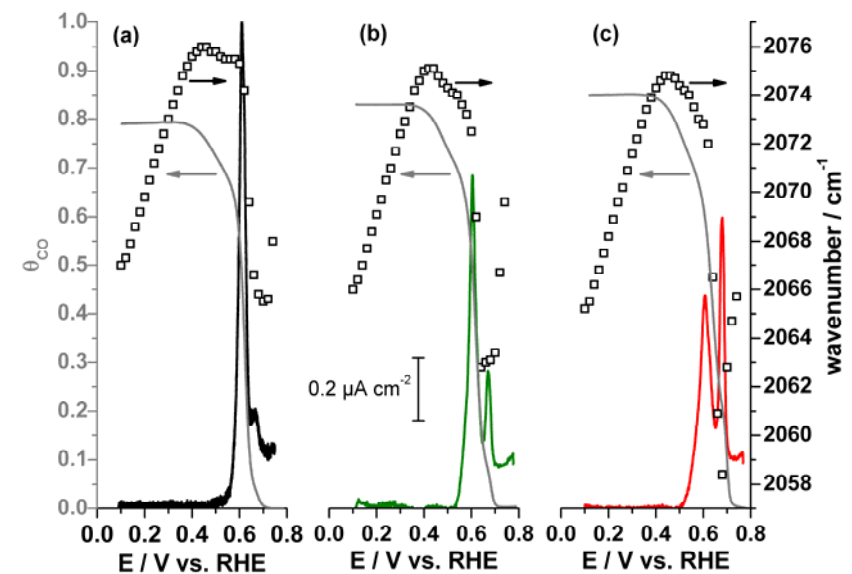
➤ hindered formic acid oxidation  $0.9 < E < 1.3 \text{ V}$     ➤ common bioxalate band

Z. Jusys *et al.*, JEAC 800 (2017) 60

# DEMS / ATR-FTRS: CO<sub>ad</sub> stripping on shape-selected Pt nanocrystals



- well ordered facets with low index orientation
- Au film as a conductive and IR enhancing support
- Quantitative CO<sub>2</sub> formation measurements
- Sulfate re-adsorption from I<sub>F</sub> and I<sub>MS</sub> difference
- Abnormal Stark effect:
  - stronger CO<sub>ad</sub> binding at lower coverage
  - CO<sub>ad</sub> compression due to sulfate adsorption

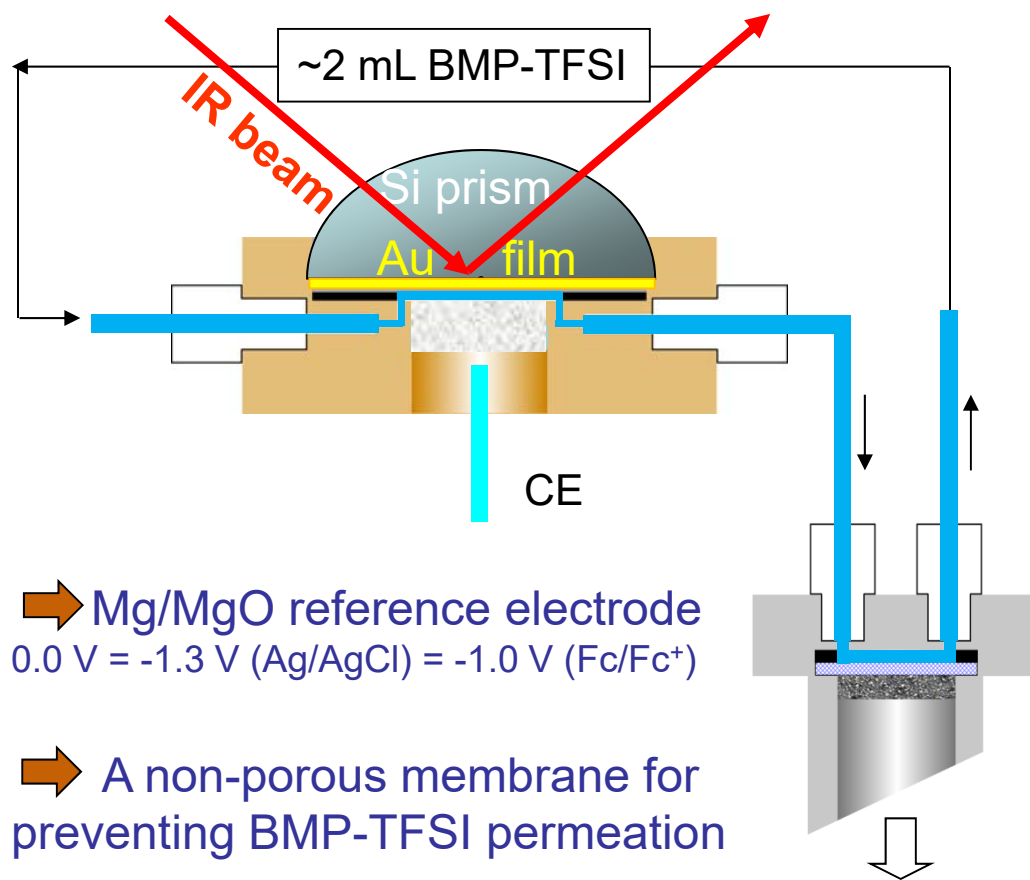


S. Brimaud *et al.*, Beilstein J. Nanotechnol. 5 (2014) 735

# ORR on Au in ionic liquid: ATR-FTIRS / DEMS flow cell

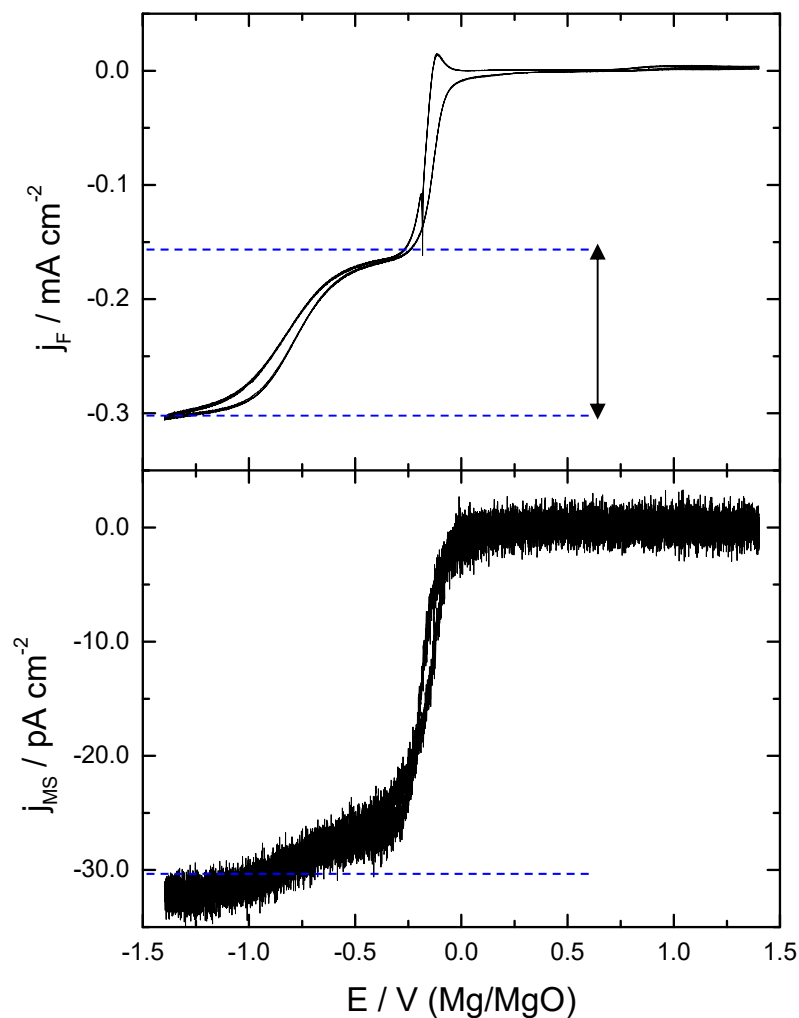


Two interconnected thin layer compartments  
(EC/ATR-FTIRS & online mass spectrometry)

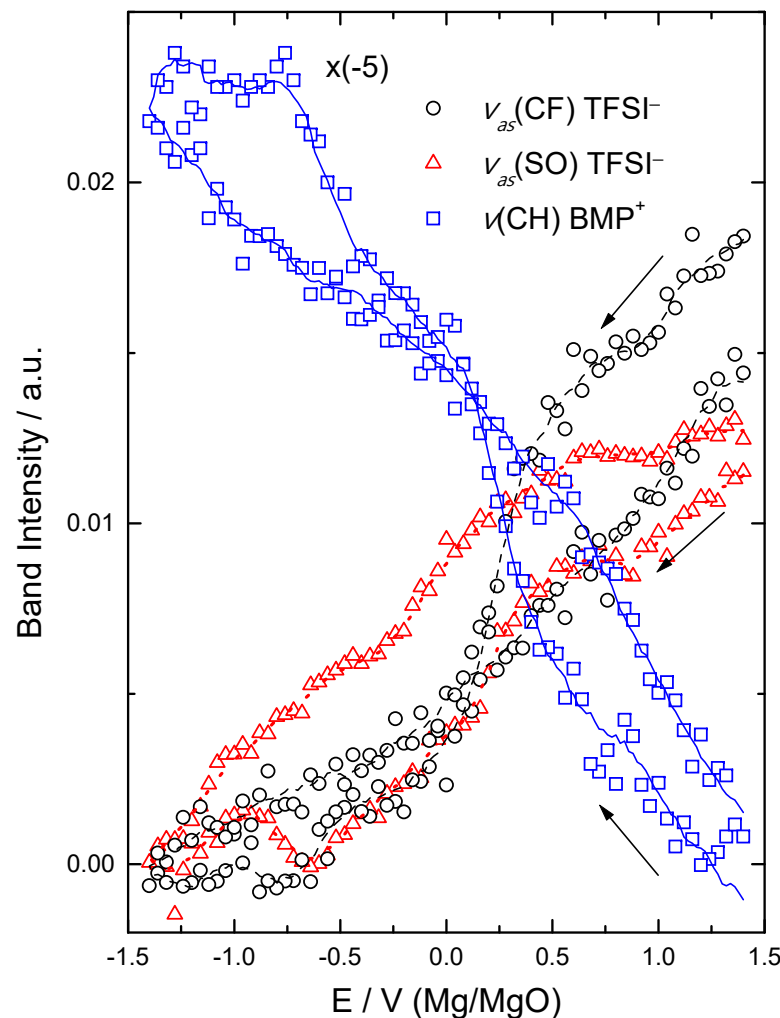




# DEMS / ATR-FTIRS: ORR at Au film electrode in BMP-TFSI

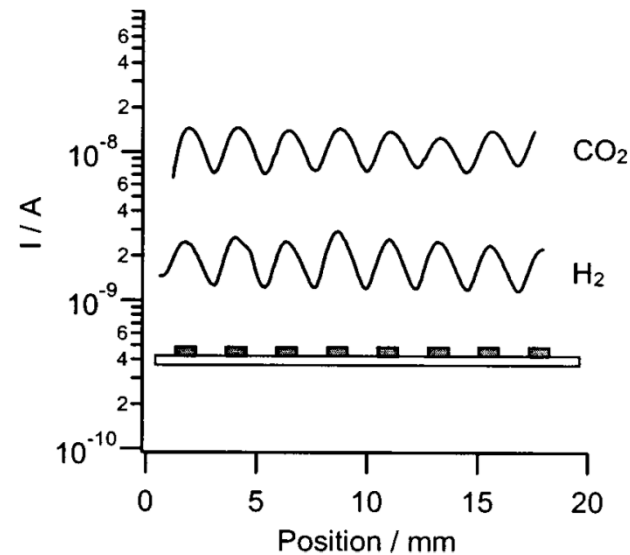
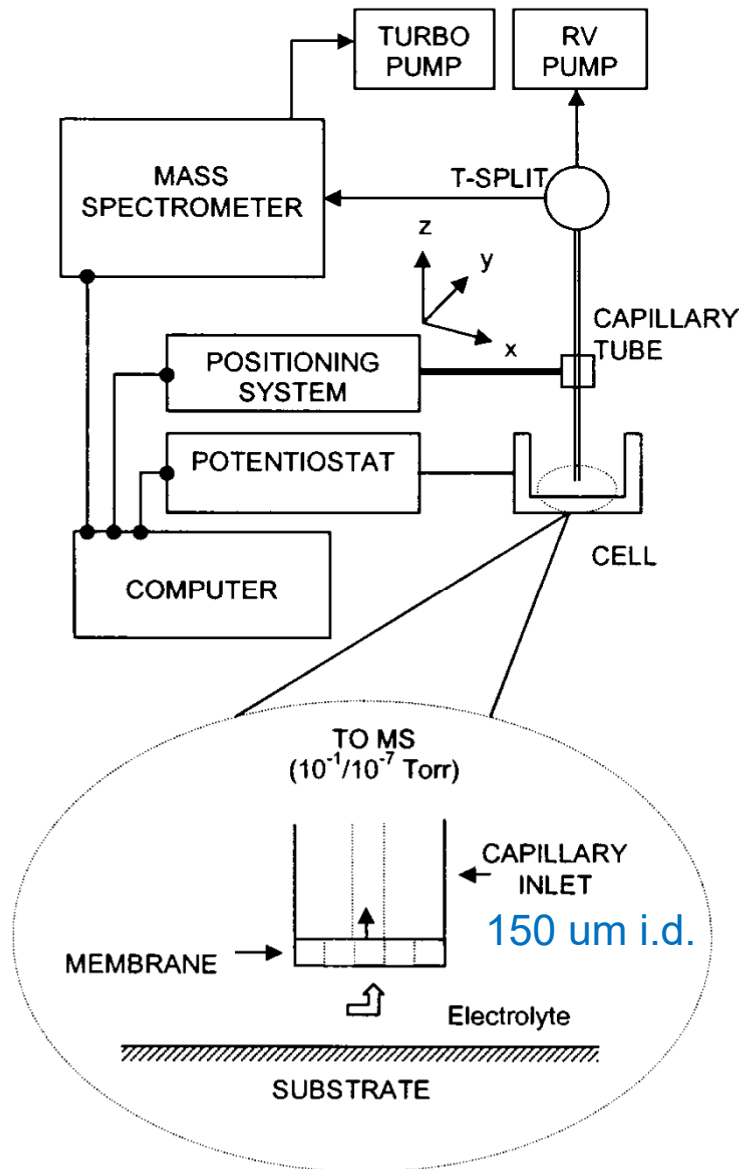


- x2 different mass transport limited currents at similar O<sub>2</sub> consumption
- ORR selectivity change from 1 to 2e<sup>-</sup>



- At low potentials cation dominates
- At high potentials anions dominates
- New anions are formed in the ORR

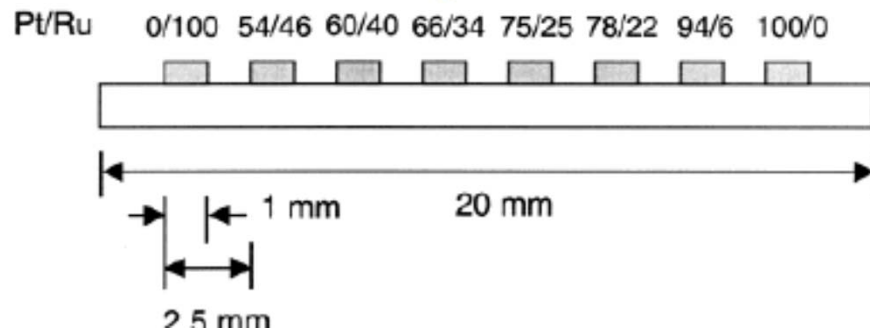
# Scanning DEMS



Ion currents for hydrogen ( $I_{H_2}, m/z = 2$ ) and  $CO_2$  ( $I_{CO_2}, m/z = 44$ ) as a function of spatial position for a capillary separation of approximately 100  $\mu m$  and a raster rate of 25  $\mu m s^{-1}$ .

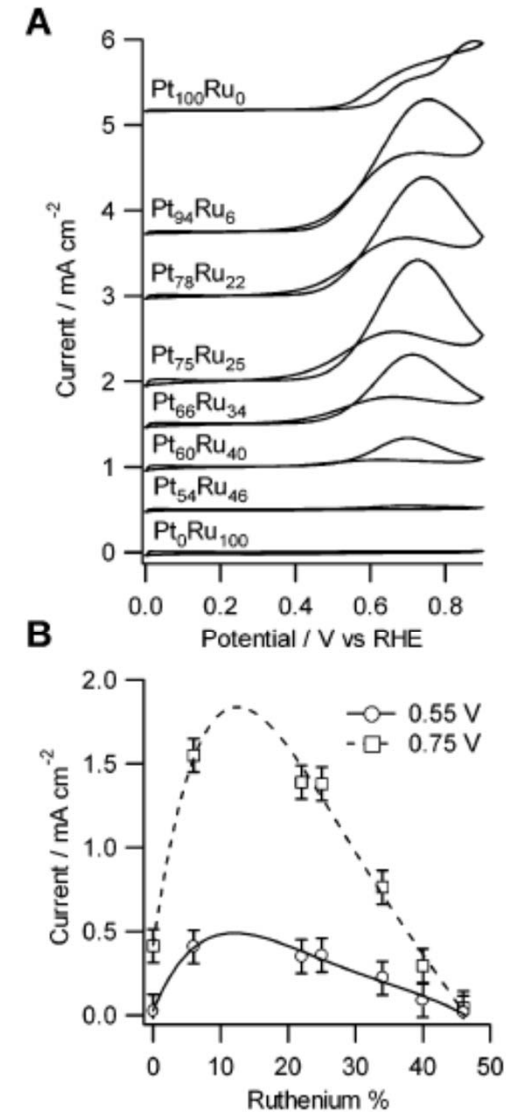
For methanol oxidation, the substrate was held at a constant potential of 0.5 V  $\sim$  vs. RHE for 15 min before imaging with the SDEMS tip. Both measurements were performed in a solution containing 1 M  $CH_3OH$  and 0.5 M  $H_2SO_4$ .

Jambunathan, K.; Hillier, A. C., Measuring electrocatalytic activity on a local scale with scanning differential electrochemical mass spectrometry. *J. Electrochemical Soc.* **2003**, 150, (6), E312-E320.



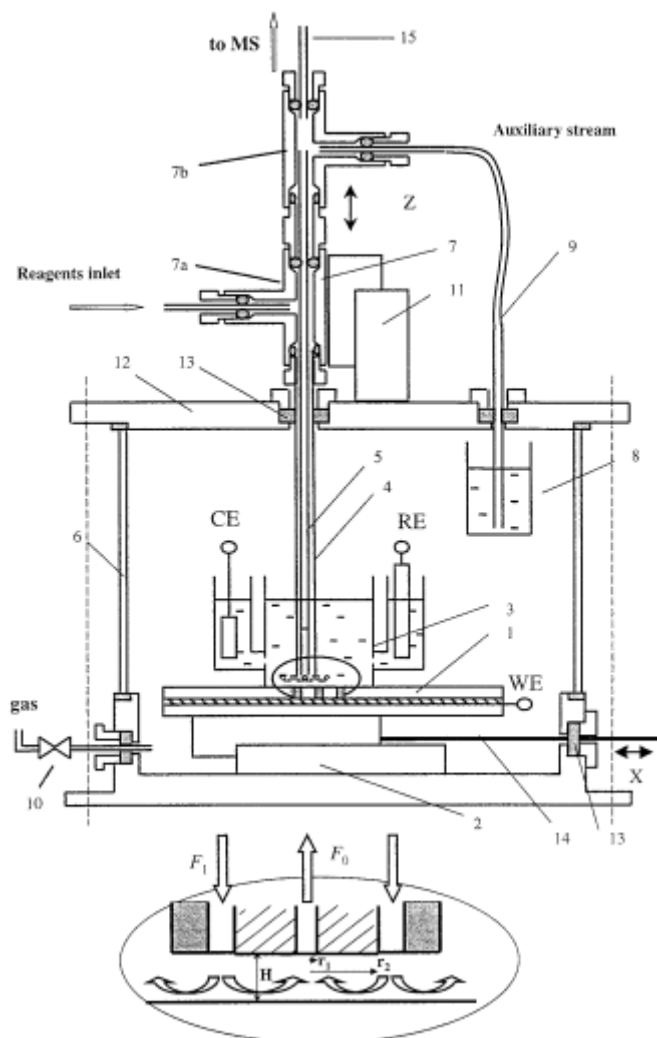
Jambunathan, K.; Jayaraman, S.; Hillier, A. C., A Multielectrode Electrochemical and Scanning Differential Electrochemical Mass Spectrometry Study of Methanol Oxidation on Electrodeposited  $\text{Pt}_x\text{Ru}_y$ . *Langmuir* **2004**, *20*, 1856-1863.

Baltruschat, J. *Jusys Tutorial: Differential Electrochemical Mass Spectrometry*.

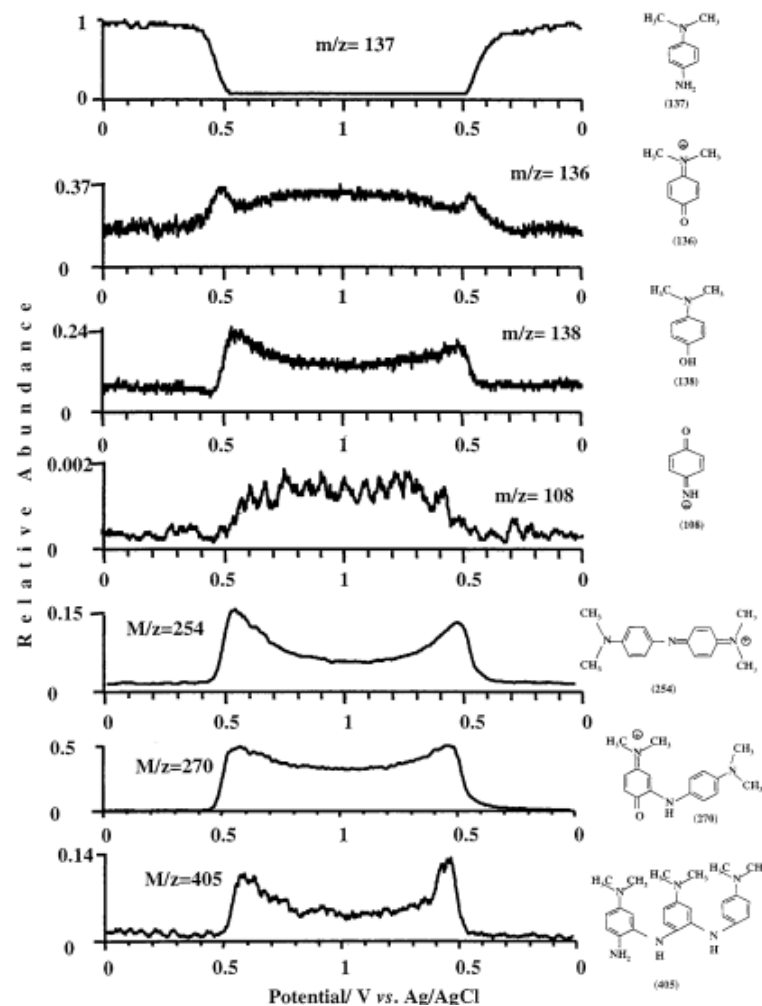


**Figure 2.** (A) Steady-state cyclic voltammetry of  $\text{Pt}_x\text{Ru}_y$  electrodes in a 1.0 M  $\text{CH}_3\text{OH}$  and 0.5 M  $\text{H}_2\text{SO}_4$  solution at 25 °C. Scan rate is 0.01 V s<sup>-1</sup>. (B) Plot of current from (A) versus ruthenium composition at substrate potentials of 0.55 and 0.75 V.

# Scanning Capillary Electrospray Ionization Mass Spectrometry



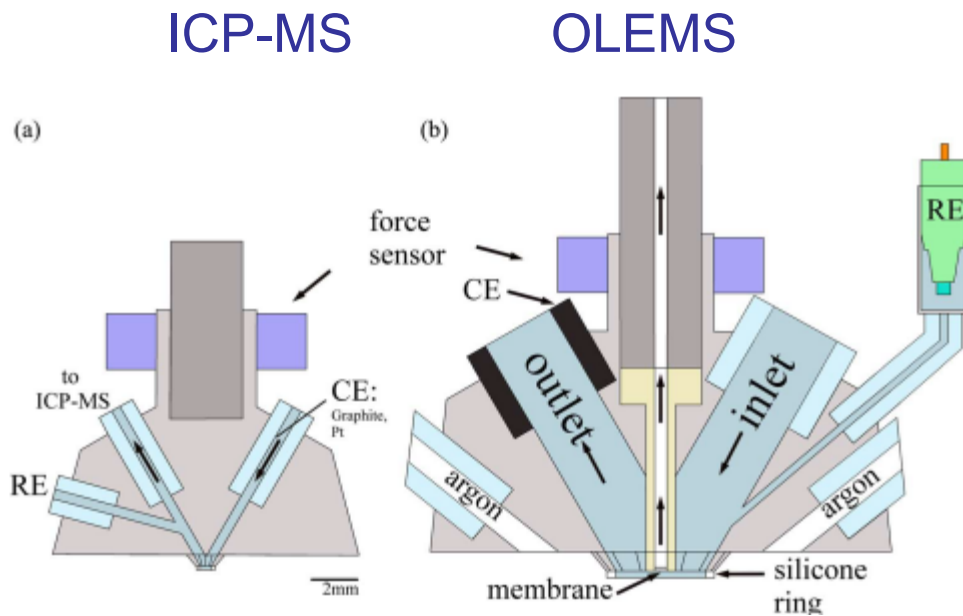
## dimethyl-p-phenylenediamine oxidation



A.D. Modestov *et al.*, *Anal. Chem.* 73 (2001) 4229

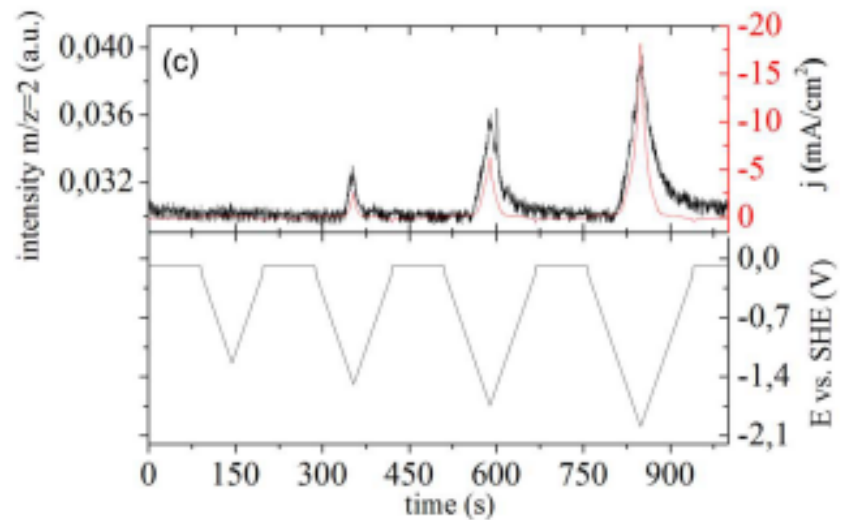
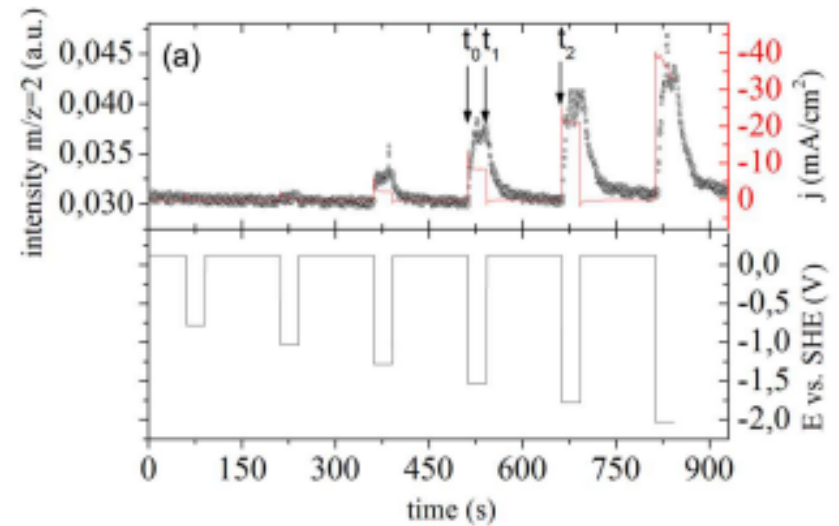
➤ Detection of non-volatile products

# Scanning flow cell (SFC): ICP-MS → OLEMS

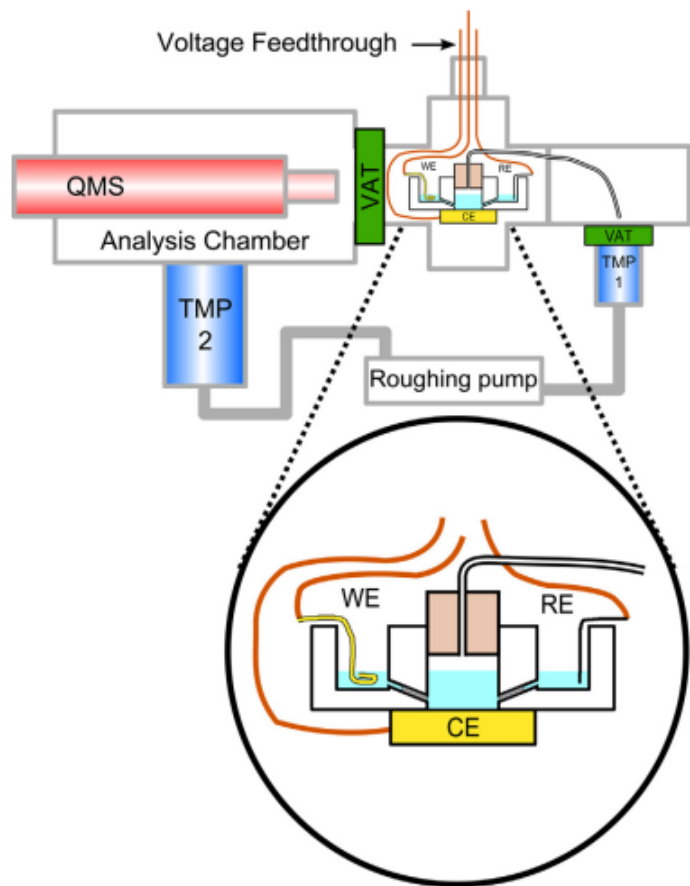


J.P. Grote *et al.*, Rev. Sci. Instrum. 85 (2014) 104101

- Versatile flow cell design
- Limited time response
- Possible ICP-MS/OLEMS combination

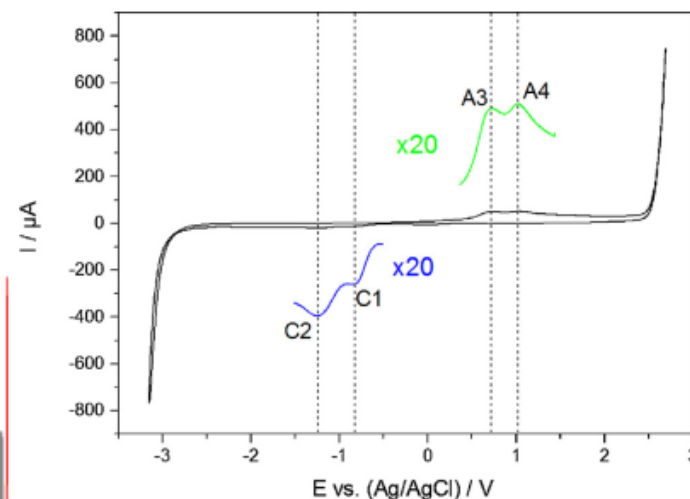


# Direct-UHV DEMS: electrochemical decomposition of ionic liquids

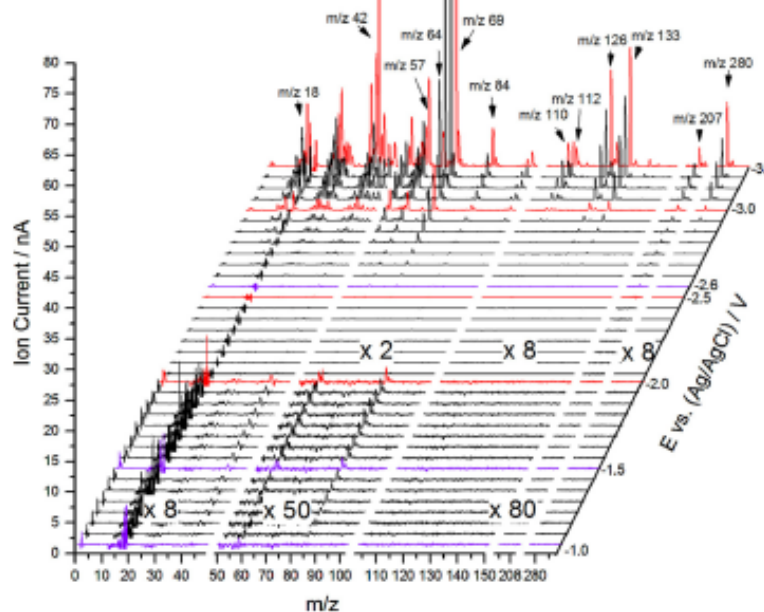


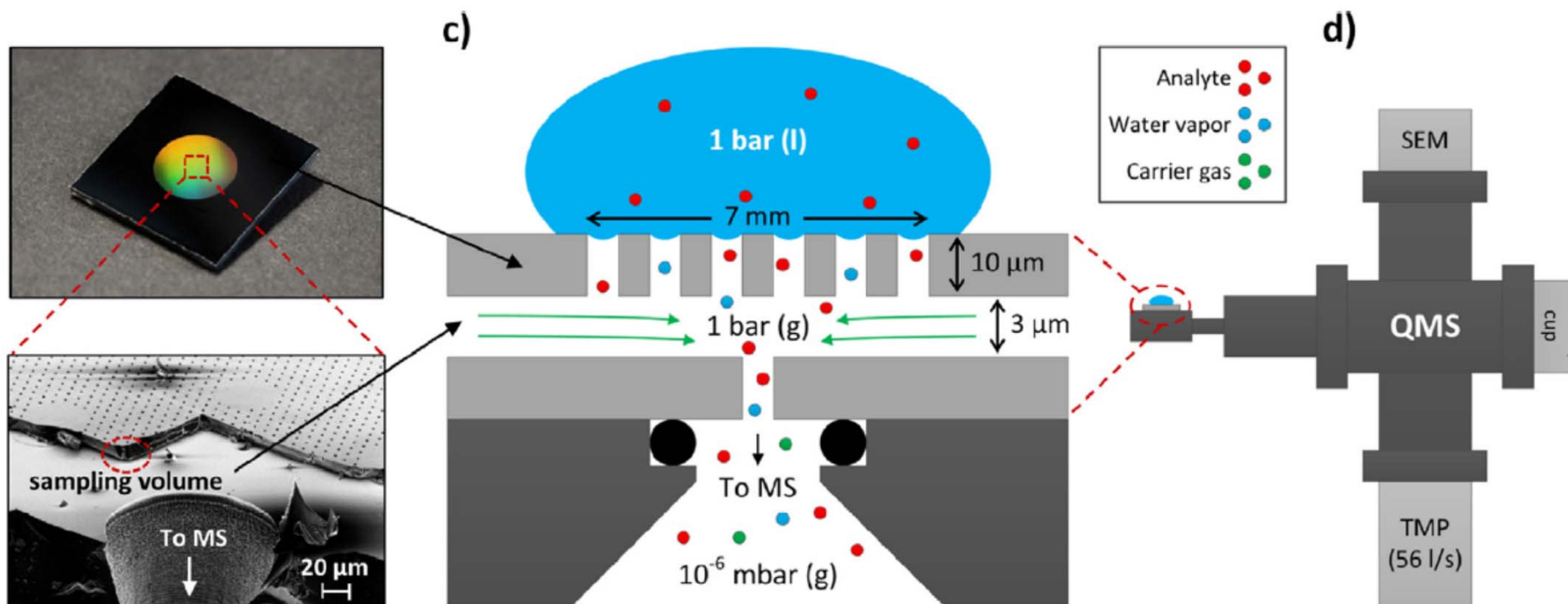
D. Alwast *et al.*, *Electrochim. Acta* 87 (2016) 290

- EC cell direct in UHV chamber
- MS analysis of decomposition
- possible for low vapor pressure



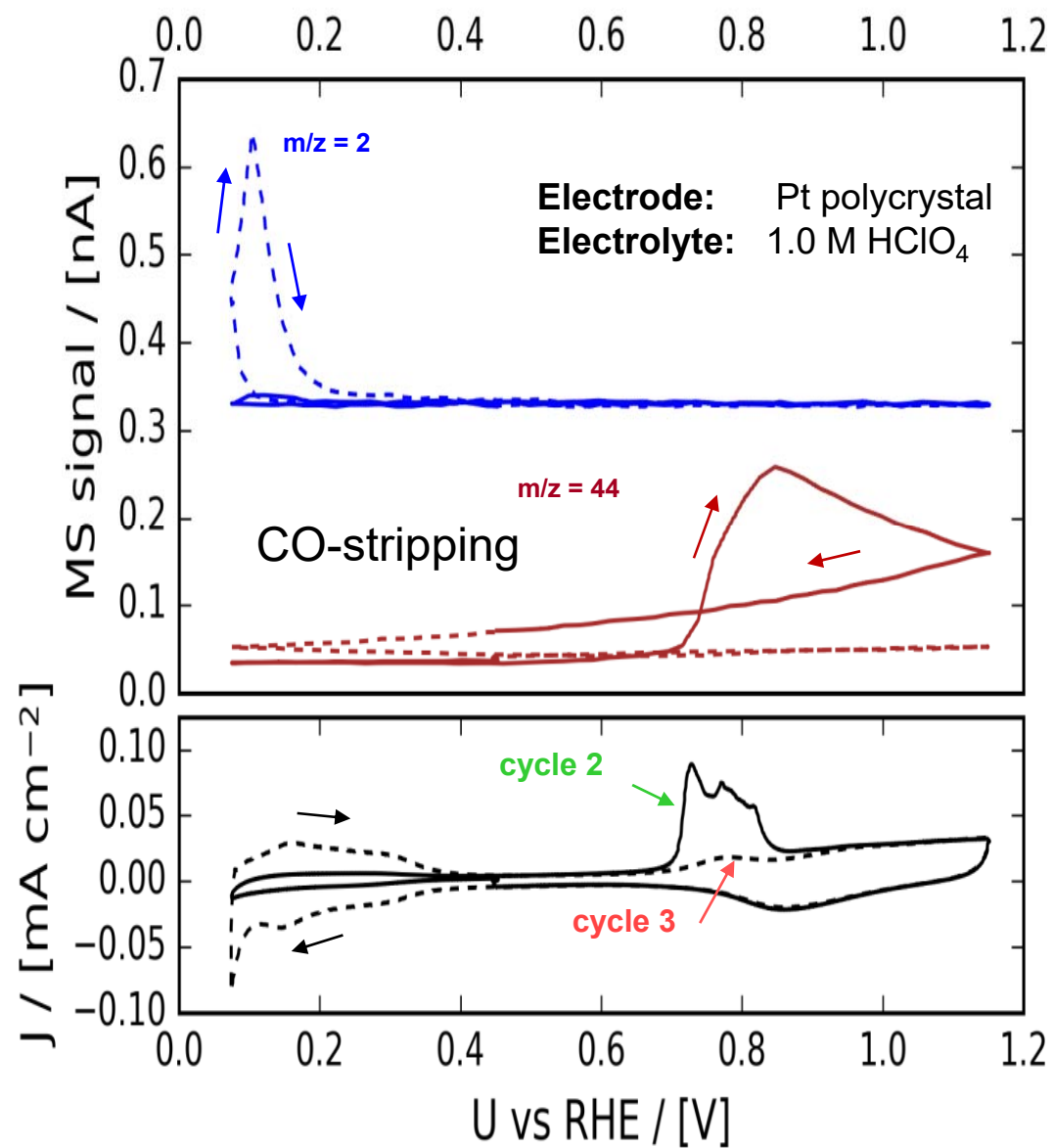
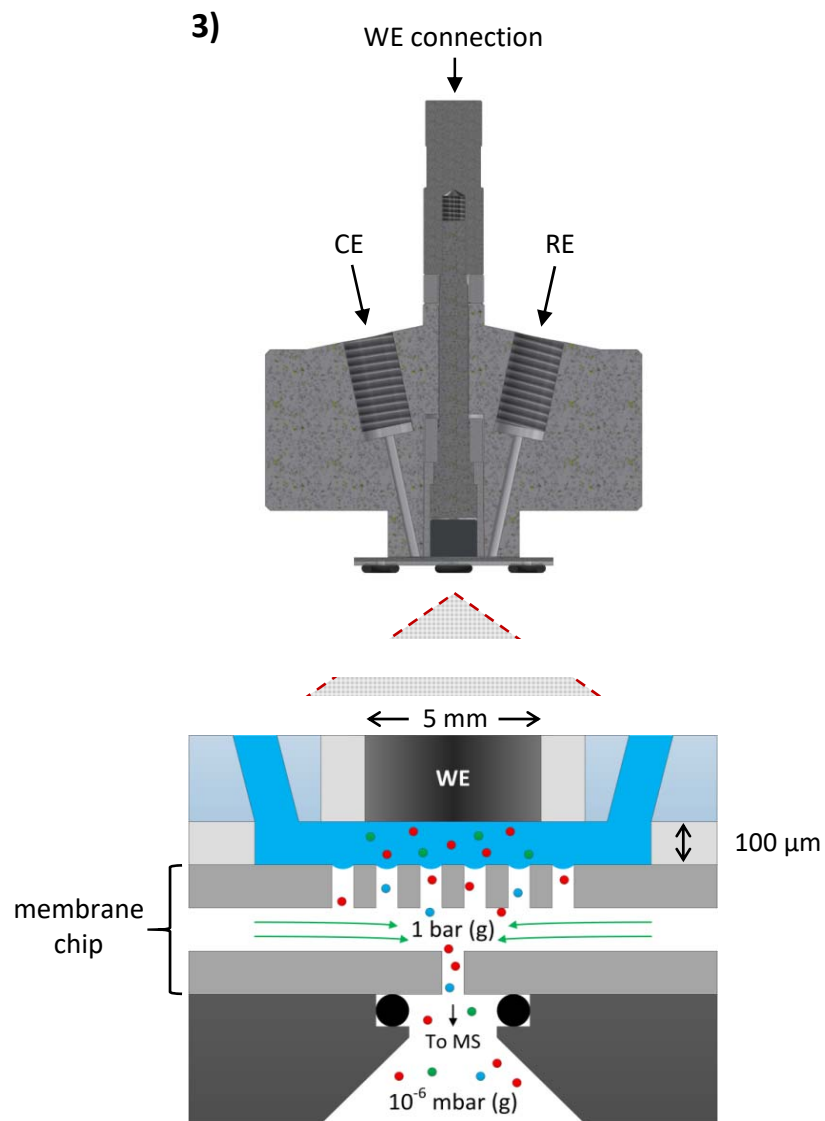
Au / [PMP][TFSI]





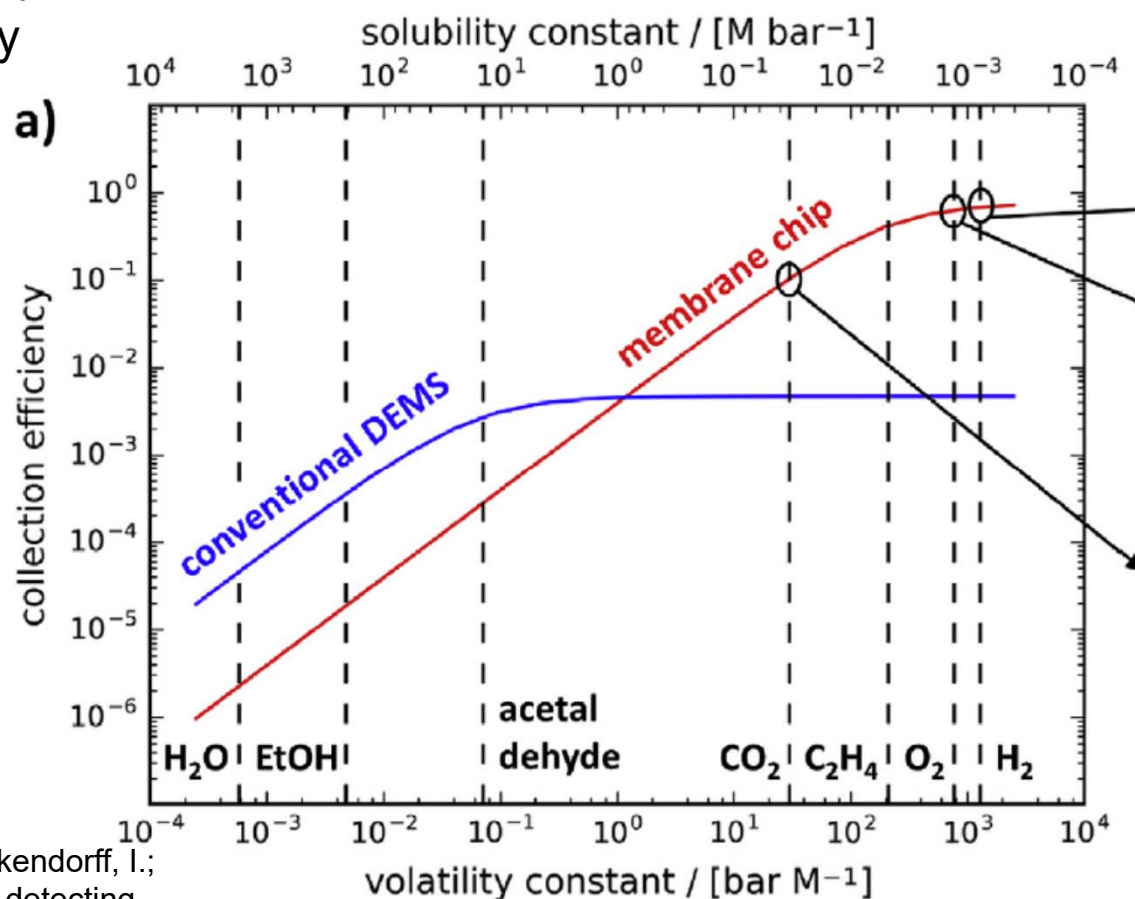
Trimarco, D. B.; Pedersen, T.; Hansen, O.; Chorkendorff, I.; Vesborg, P. C. K., Fast and sensitive method for detecting volatile species in liquids. *Review of Scientific Instruments* **2015**, 86, (7).

Trimarco, D. B.; Scott, S. B.; Thilsted, A. H.; Pan, J. Y.; Pedersen, T.; Hansen, O.; Chorkendorff, I.; Vesborg, P. C. K., Enabling real-time detection of electrochemical desorption phenomena with sub-monolayer sensitivity. *Electrochimica Acta* **2018**, 268, 520





membrane collection efficiency  
 X vacuum collection efficiency



Trimarco, D. B.; Pedersen, T.; Hansen, O.; Chorkendorff, I.; Vesborg, P. C. K., Fast and sensitive method for detecting volatile species in liquids. *Review of Scientific Instruments* **2015**, 86, (7).

# Conclusion

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- DEMS is a versatile, sensitive, (semi-)quantitative method for the detection of volatile products
- Various kinds of cells for different applications
- Detection of adsorbates, intermediates, products
- Elucidation of reaction mechanisms
- DEMS is a vital technique which is still developing
- It's versatility allows for various purpose-oriented combinations
- Further method development is based on the enthusiasm and creativity