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Differential Electrochemical Mass Spectroscopy(DEMS): New Insights

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- Introduction
- Different types of DEMS cells
- Application of DEMS
- Ex.1: MeOH (oxidation, mechanism, kinetic, catalyst effect and ads. rate)
- Ex.2: Effect of surface structure on the electrooxidation of ethanol
- Ex.3: ORR and OER in aprotic electrolyte
- Conclusions

2

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History

Bruckenstein, S., Rao, R. and J. Gadde, J. Am. Chem. Soc. 93(1971)793.
Brucken … 4)285.

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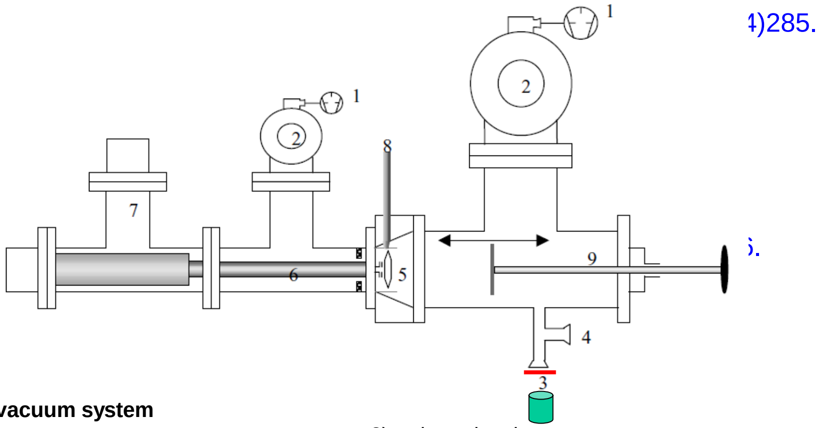

The vacuum system

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

3

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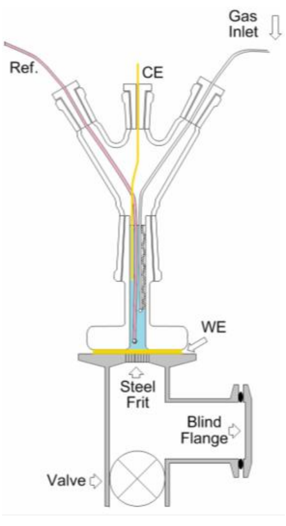
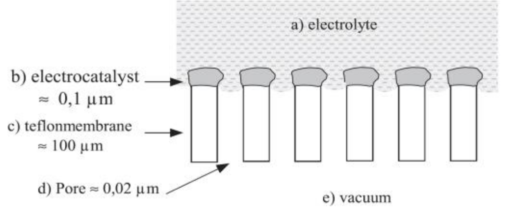
The Conventional Cell



- Detection of Volatile products.
- Electrochemical cell connected to high vacuum systems of MS via pourous Teflon membrane.
- Teflon membrane prevents the transport of solution species to the system.
- Delay time ~0.1 s

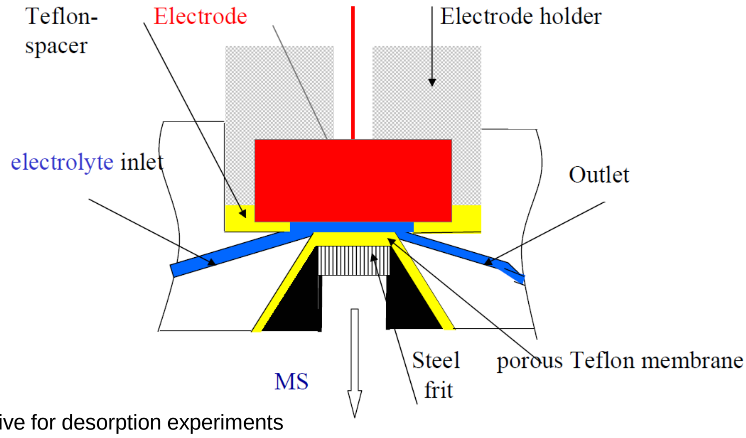
- no single crystals, no massive electrodes
- depletion of gaseous reactants due to evaporation



- Collection Eff. is 0.9 for sputtered electrode
- Model for GDE

4

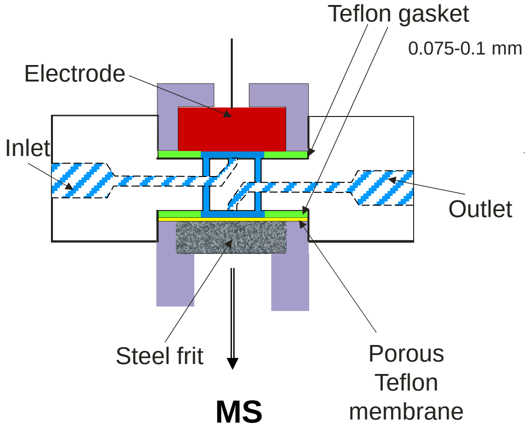
Thin layer cell for DEMS

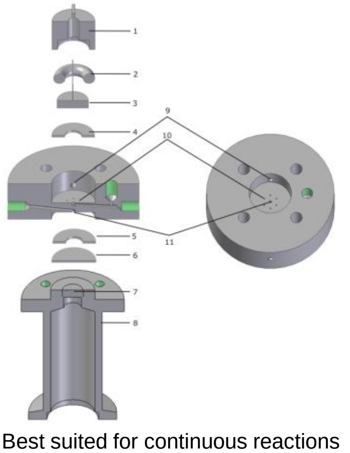


Sensitive for desorption experiments
(transfer coefficient N~0.9)
Unsensitive for continuous reactions

Hartung, T. and H. Baltruschat Langmuir 6(1990)957.

Dual-thin-layer flow-through cell





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

Z. Jusys, H. Massong, H. Baltruschat, *J. Electrochem. Soc.* 146*(1999)*1093.

6

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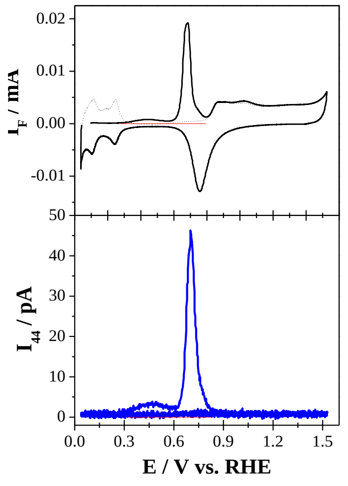
DEMS Calibration

Example: $CO_{ad} + H_2O \Rightarrow CO_2 + 2e^- + 2H^+$



$$K^*_{CO_2} = z\frac{Q_{MS}}{Q_F}$$

$$K^*_{H_2}$$

$$K^*_{O_2}$$

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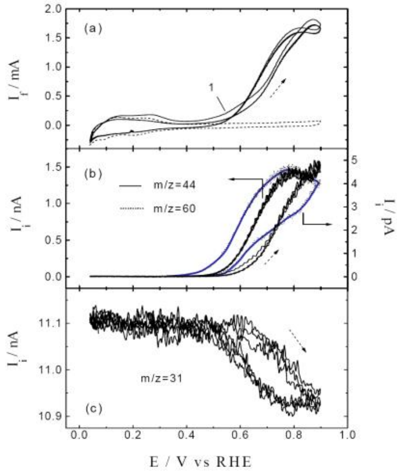
Electrooxidation of bulk methanol



0.1 M methanol @ nonoparicles of Pt supported on GC

$A_{44}\% \sim 90\%$

$E_{Methylformate} < E_{CO2}$

Wang and Baltruschat, J. Electroanal. Chem., 2001, 509, 163.

10

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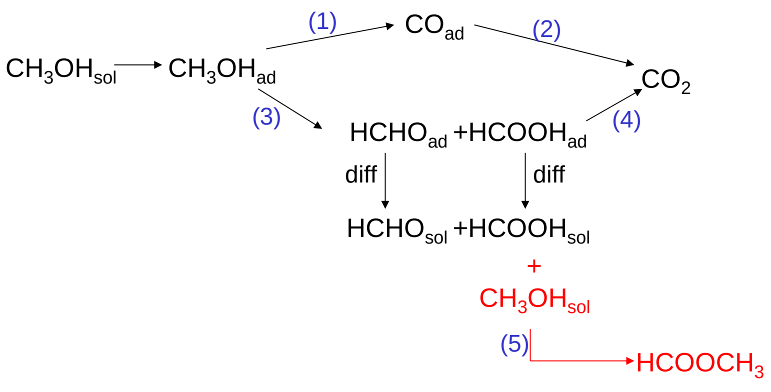
Electrooxidation of methanol

Dual pathway mechanism



Is methylformate an indicator for HCOOH ??

11

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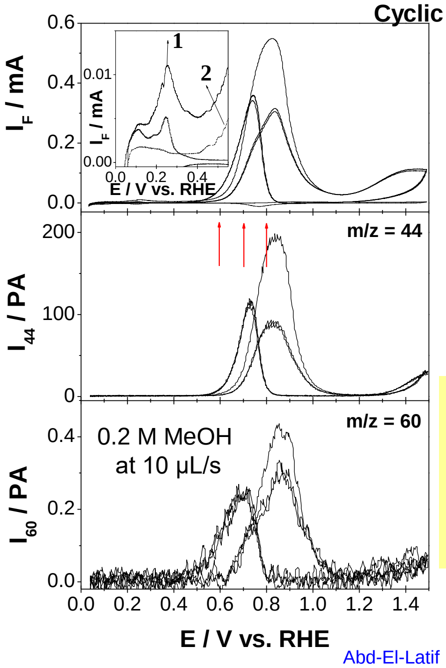
Electrooxidation of methanol at Pt(pc)

Cyclic voltammetry



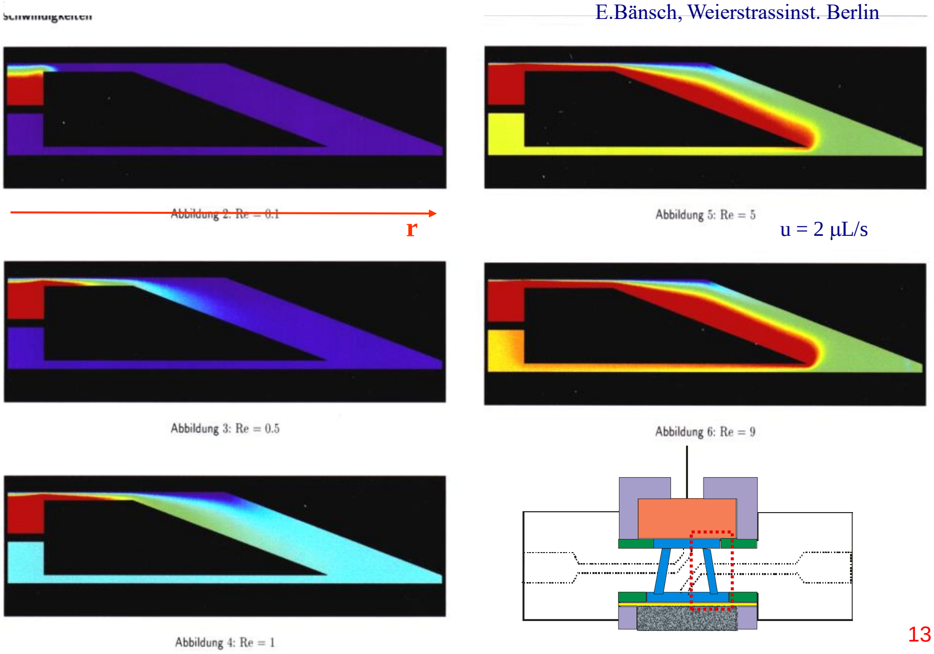
u/ (µL.s^{-1})	0.1 M MeOH		0.2 M MeOH	
	A_{44}%	A_{60}%	A_{44}%	A_{60}%
1.6	32	0.72	25	1.4
5	32	(1.2)	28	(2.6)
10	31.1	n.d	27	(3.8)
30	30.5	n.d	24	n.d.

- A_{44}: hardly depends on u
  : decrease with MeOH conc. ⟺ poisioning.
  : < 40% ⟺ Ald + F.A formation.
- A_{60}: increase with u ⟺ incomplete mixing.
  : increase with MeOH conc. ⟺ 2 MeOH molecules for methylformate formation.

Abd-El-Latif and Baltruschat, J. Electroanal. Chem. 662(2011)204

Dual Thin layer cell: Numerical simulation of diffusion

E.Bänsch, Weierstrassinst. Berlin



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Electrooxidation of methanol at Pt(pc)

Potential step

u/(µLs^{-1})	E_{ads}/ V	0.1 M MeOH		0.2 M MeOH	
		A_{44}%	A_{60}%	A_{44}%	A_{60}%
1.6	0.6 0.7 0.8	17.5 28 35	1 0.74 0.7	14.7 23.3 31.2	3.2 1.7 1.5
5	0.6 0.7 0.8	19.2 30.5 36	(2.4) (1.3) (1.3)	10.7 23.2 31.3	(3.7) (2.3) (2.5)
30	0.7	27.6	(1)	20	(1.2)

- A_{44}: increase with potential ⟺ faster oxidation of CO_{ad}.
  : decrease with MeOH conc. ⟺ poisioning.
- A_{60} increases with decreasing E_{ads} and with increasing the MeOH conc.
- Methylformate formation: reaction order >1.5 ⟺ 2 MeOH molecules are required.

Abd-El-Latif and Baltruschat, J. Electroanal. Chem. 662(2011)204

14

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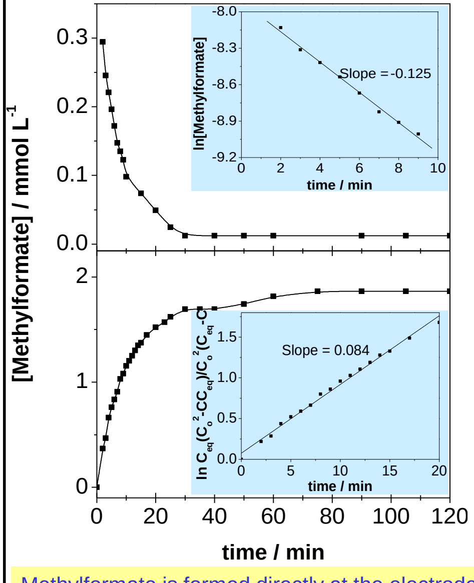
Methanol oxidation

Kinetics of methanol esterification



$$HCOOCH_3 + H_2O \underset{k_{-1}}{\overset{k'_1}{\rightleftharpoons}} CH_3OH + HCOOH$$

10^{-3} M Methylformate in 0.5 M H_2SO_4

$\ln[C] = \ln[C_o] - k_1 t$ =>

$k_1 = 2.26 \times 10^{-3}\ s^{-1}$ ⟺ $\tau = 440$ s

0.2 M MeOH + 0.2 M HCOOH in 0.5 M H_2SO_4

$$t = \frac{C_{eq}}{k_{-1}\left(C_o^2 - C_{eq}^2\right)} \cdot \ln \frac{\left[C_{eq}\left(C_o^2 - CC_{eq}\right)\right]}{\left[C_o^2\left(C_{eq} - C\right)\right]}$$

At [MeOH] = 0.1 M =>

$k_{-1} = 6.6 \times 10^{-6}\ s^{-1}$ ⟺ $\tau = 150 \times 10^3$ s

$\tau \approx 5$ s for the dual thin layer cell at 1.6 µL/s

Methylformate is formed directly at the electrode surface and not in solution phase

Abd-El-Latif and Baltruschat, J. Electroanal. Chem. 662(2011)204

15

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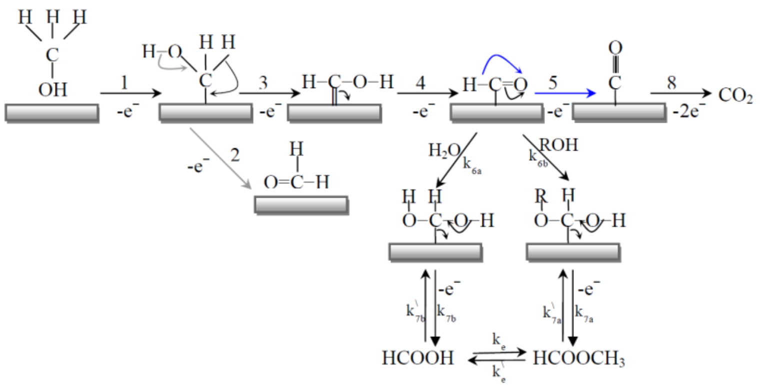
Mechanism of methylformate formation



The nucleophilic power of oxygen atom in methanol molecule is higher than that of water

Abd-El-Latif et al. Trends in Anal. Chem. 70(2015)4

16

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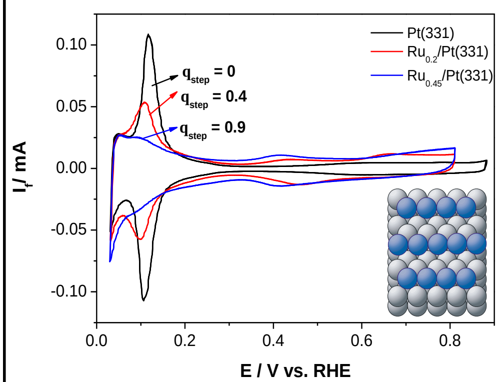
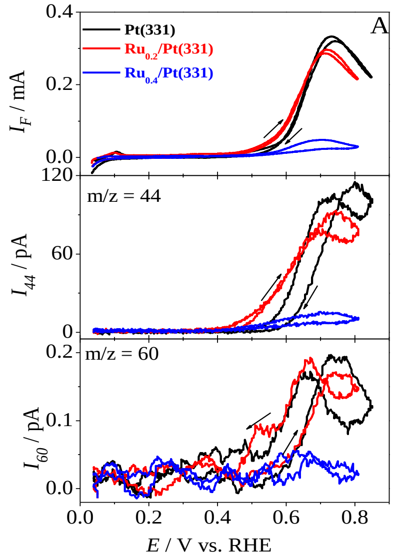
Electrooxidation of Methanol on Ru/Pt(331)



Cyclic Voltammetry for Pt(331) in 0.1M H_2SO_4 + 0.5M $HClO_4$ at 50 mV/s before and after Ru deposition



Partial step decoration: -ve shift in the onset Potential => Electronic & bifunctional effects
Full step decoration: catalytic activity decreases=>free Pt sites at steps are important

17

Effect of Ru and surface structure on MeOH adsorption rate

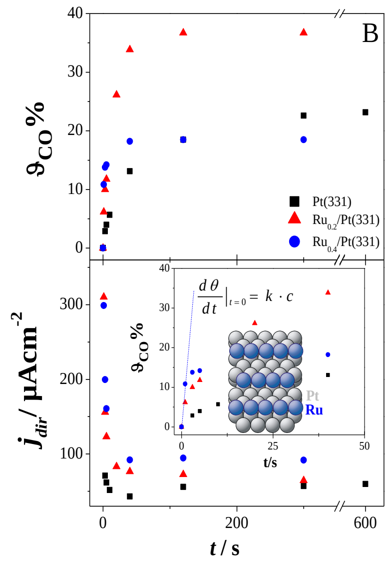


Table 3. Rates of methanol adsorption (determined for $t_{ad}^{min} = 1$ s) together with the relative and steady-state methanol adsorbate coverages at different platinum surfaces and different adsorption potentials.

Surface	E_{ad} [V] (vs. RHE)	r_{ad} [MLs^{-1}]	$\vartheta^{max}_{CO(MeOH)}$ [%]
Pt(331)	0.35	0.01	22.5
	0.45	0.03	31
	0.65	0.06	12
$Ru_{0.2}$/Pt(331)	0.35	0.06	37
$Ru_{0.4}$/Pt(331)		0.1	19
Pt(332)	0.45	0.01	–
Pt(100)	0.3	0.022	–
Pt(11,1,1)		0.018	–
Pt(pc)	0.3	0.1	20

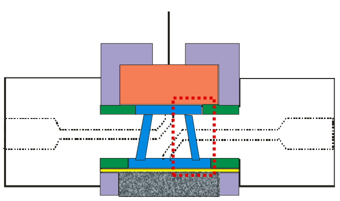
$$\frac{d\theta}{dt}\Big|_{t=0} = k \cdot c$$

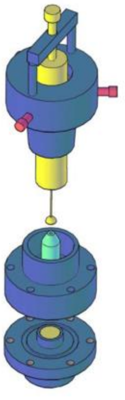
Mostafa et al. ChemPhysChem. 15(2014)2029

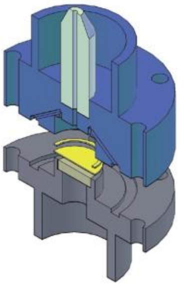
18

New DEMS cell for bead crystal

- Dual thin layer cell: Pressure on the single crystal ⟷ defects.
- Bead crystals: usual hanging mensicus configuration. ⟷ a new DEMS cell.







Advantage:
- bead single crystals (2-3 mm).
- Hanging meniscus configration.
- Defined convection.

- Electrolyte flow rate: equal at inlet and outlet.
- Distance between the electrode surface and glass capillary: ~ 200 µm.

Abd-El-Latif, et al. Electrocatal., 2012, 3, 39.

19

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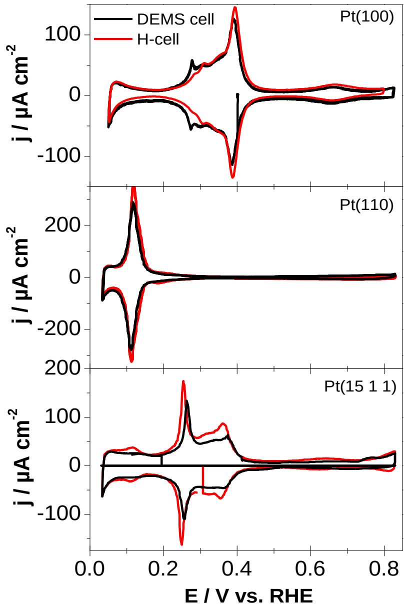
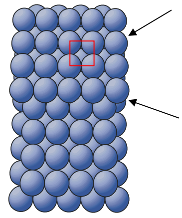
Characteristic CVs for bead Pt(hkl)



Pt(711) = Pt(S)[4(100)x(111)]



❑ DEMS cell: flowing electrolyte: high quality CVs as in stagnant solution.

20

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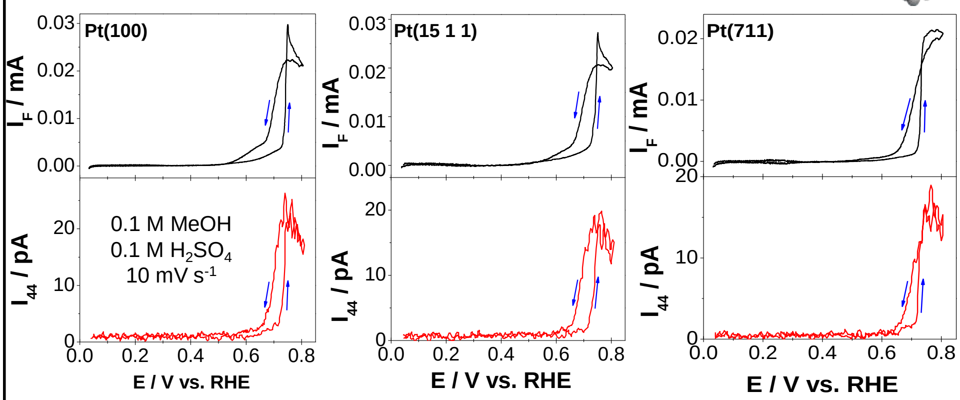
Electrooxidation of MeOH at bead Pt single crystals



Electrode	Pt(100)	Pt(15 1 1)	Pt(711)
A_{44} @ 0.8 V	46	40	35

• A_{44} decreases with increasing the step density ➡ lower activity of monoatomic (111) step towards the indirect pathway.

• The number of (100) does not change much ➡ a geometric ensemble effect at stepped surfaces.

21

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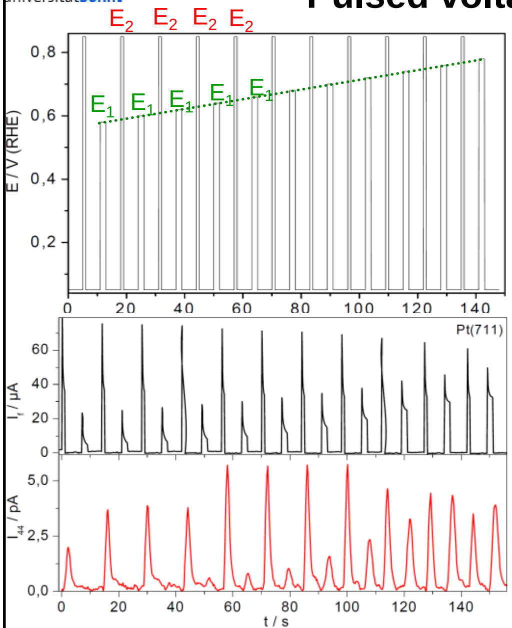
Pulsed voltammetry



E_{ad}/V	Pt(100)	Pt(15 1 1)	Pt(711)
0.58	0	9	6
0.6	0	11	7
0.62	25	12	10
0.64	28	12.5	12
0.66	40	16	11
0.68	50	20	15
0.7	74	30	21
0.72	84	42	26
0.74	84	62	29
0.76	89	63	35

- At 0.85 V: complete oxidation of methanol adsorbate species (CO_{ads}).
- A_{44} decreases with increasing the step density.
- Free and large (100) terrace sites are important for the complete oxidation of methanol to CO_2.

•Abrupt change in the I_{44} even in 1 s ⟹ fast response.

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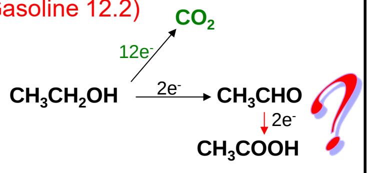
Ethanol as an alternative fuel in fuel cells

- Available from renewable resources (Annual EtOH production:85.2 million litres in 2012)
- Easy storage and Low toxicity
- The total oxidation reaction produce 12 e^- / molecule
- High energy density (8.1 kWh/kg) (Methanol ≈6.1) (Gasoline 12.2)



Challenges

- Lack of a catalyst that can initiate complete oxidation
- Ethanol oxidation to CO_2 is associated with the cleavage of the C-C bond, which requires a higher activation energy than C-H bond breaking

24

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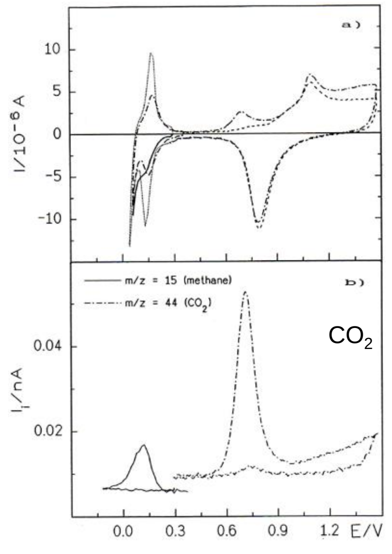
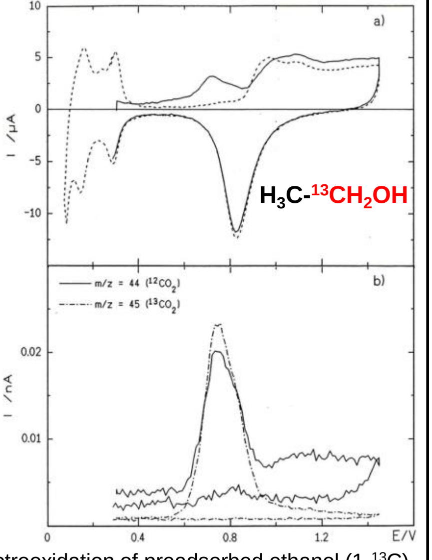
Electrooxidation of adsorbed ethanol



Cathodic desorption of preadsorbed ethanol from Pt(ll0) and subsequent oxidation of the remaining adsorbate $\boldsymbol{E_{ad}}$ = 0.3V.

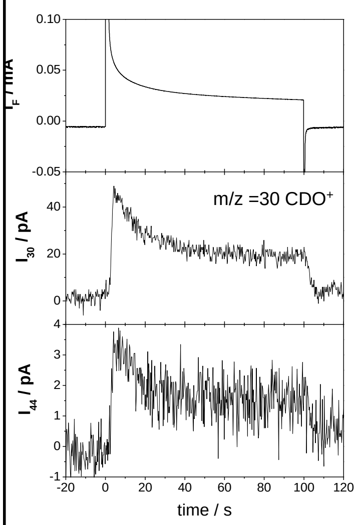


Electrooxidation of preadsorbed ethanol (1-^{13}C) on polycrystalline Pt at E_{ad}=0.3V

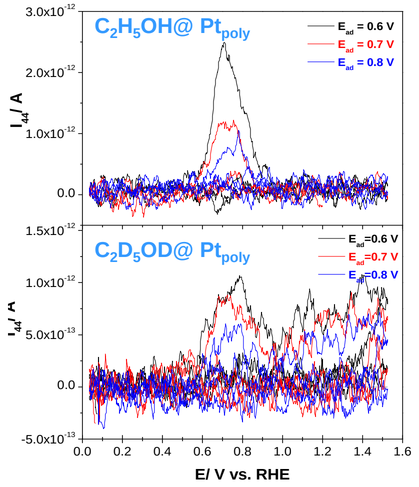
Schmiemann, Müller and Baltruschat, Electrochimica Acta, **40**(1995)99.

Thin-layer cell 25

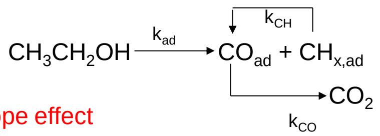
Potential step experiment on Pt(pc)



A% = 7



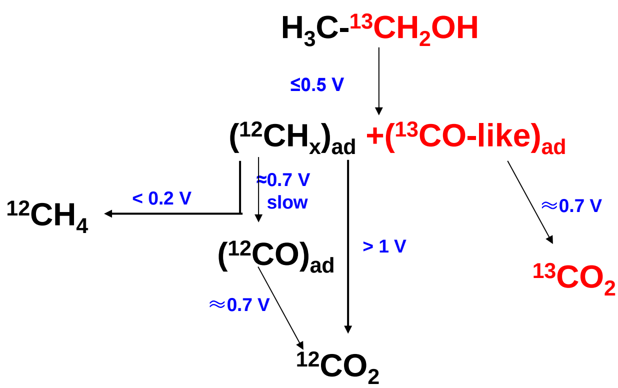
Potential step experiment at 0.7 V vs. RHE
for 0.01 M C_2D_5OD on Pt(PC) at 5 μL/s



Kinetic isotope effect

26

Reaction scheme



Schmiemann, Müller and Baltruschat, Electrochimica Acta, **40**(1995)99.

27

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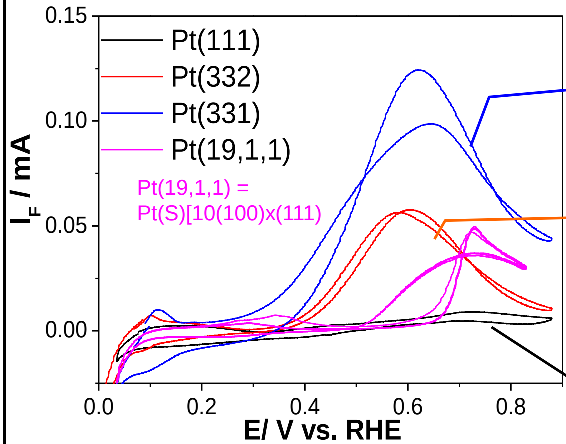
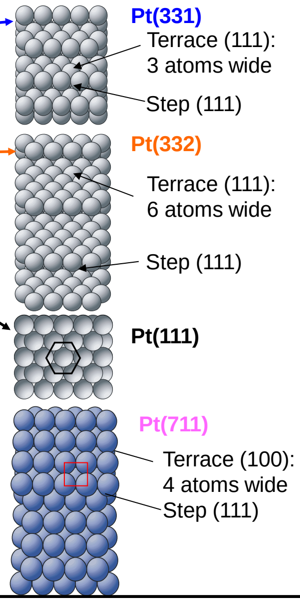
Effect of surface structure on EtOH oxidation





10^{-2} M EtOH in 0.1M H_2SO_4 + 0.5M $HClO_4$
@10 mV/s and 5 µL/s

- Pt(111): very low catalytic activity for EtOH oxidation.
- Increasing the step density ⟺ increasing activity
  ⟺ electrooxidation of EtOH at step sites

28

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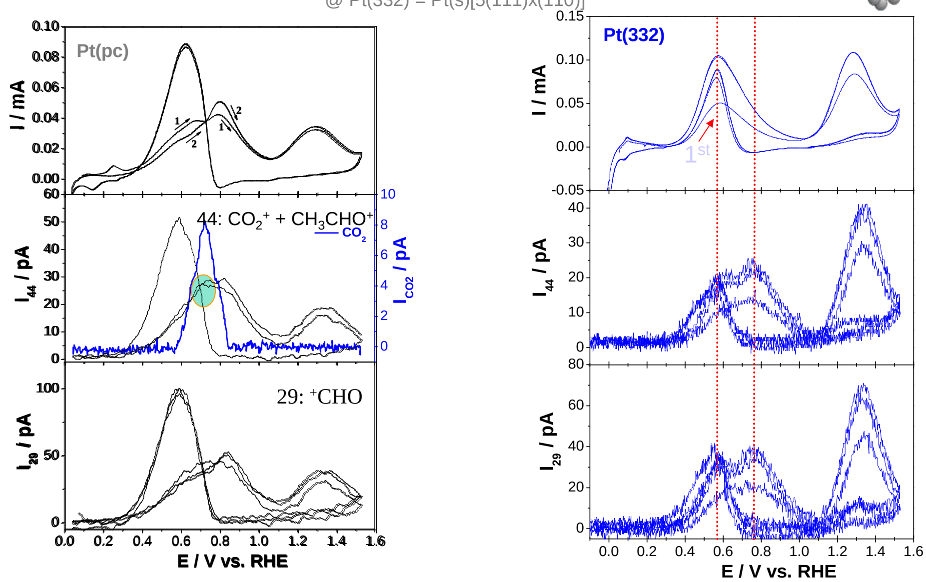
Electrooxidation of ethanol
@ Pt(332) = Pt(s)[5(111)x(110)]



10^{-2} M ethanol in 0.1M H_2SO_4 + 0.5M $HClO_4$ at 5 µL/s

Reactivity at roughened stepped surfaces higher than at pc Pt
Pt(332): different shape of CV and MSCV

$^{CH_3CHO}I_{44}$ = 0.55 $^{CHO}I_{29}$

29

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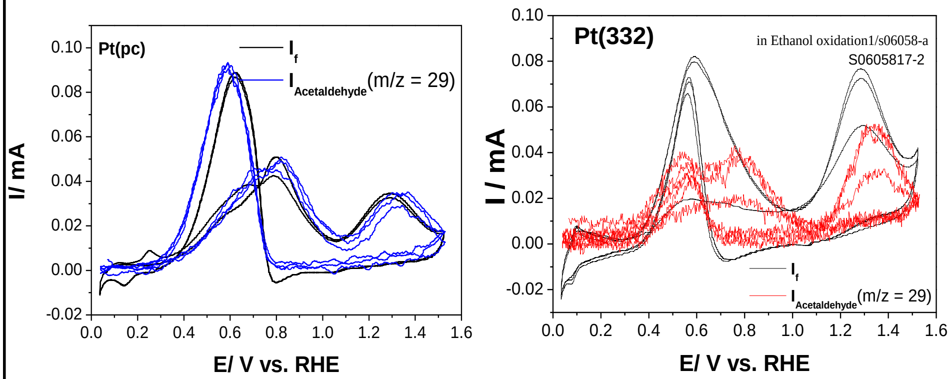
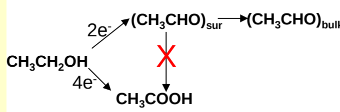
The current efficiency for acetaldehyde



Comparison of faradaic current with ion current of acetaldehyde

Giz, M. J. and Camara G. A. J, Electroanal. Chem. 625(2009)117.

- Pt(pc): acetaldehyde is the main product (Curr.eff. ≈100%) and it is independent of potential.
- Pt(332): 1- at 0.6 V: I_F exceeds the formation of acetaldehyde (direct formation of acetic acid) (separate pathway)
  2- at 0.8 V: only formation of acetaldehyde (Curr. eff. ≈100%).



30

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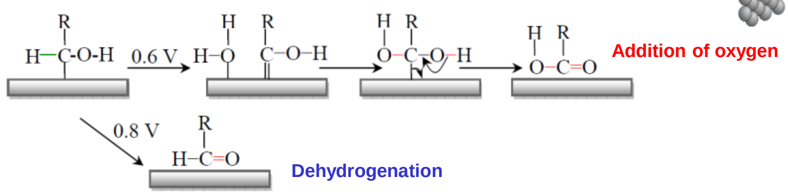

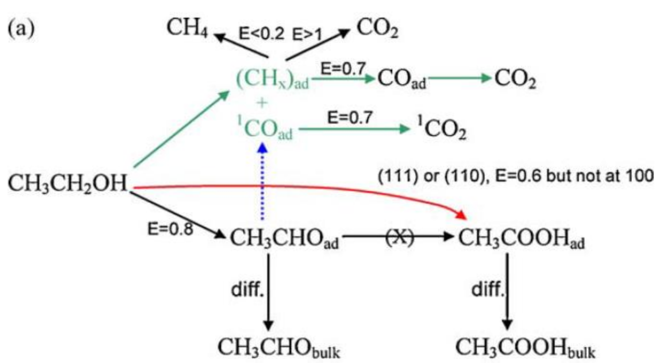

Abd-El-Latif et al. Electrochimica Acta **55** (2010) 7951.

31

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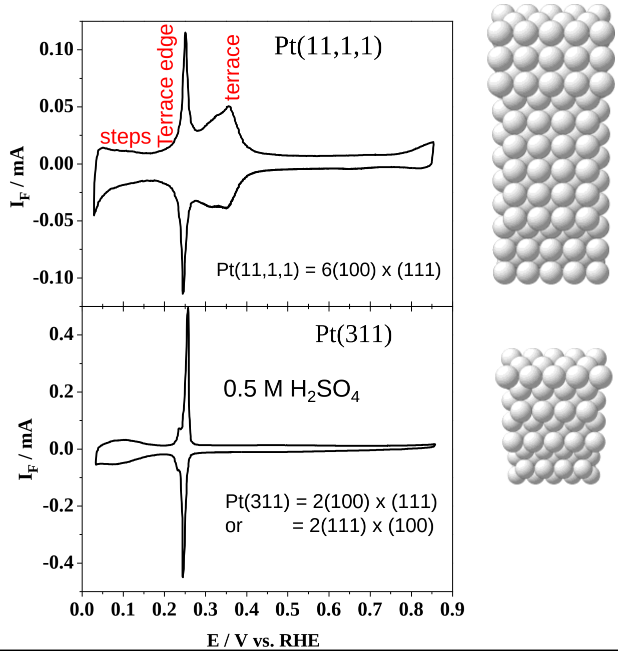
Pt stepped single crystals vicinal to (100)



32

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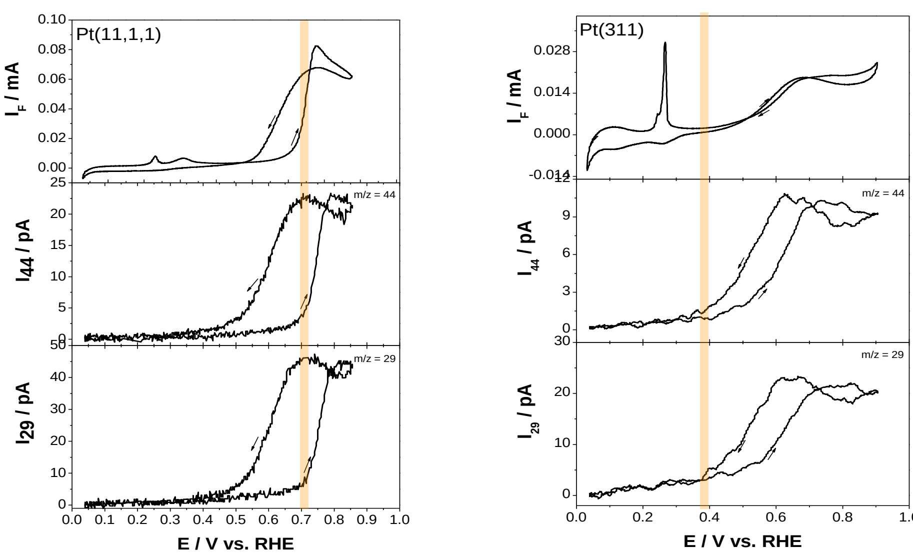

Pt(311) similar to surfaces vicinal to (111) planes

33

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Current efficiencies

Surface	Cycle Nr.	A_{44}%	A_{29}%
s-Pt(11,1,1)	1	0	100
	2	0	100
r-Pt(11,1,1)	1	0	100
	2	0	100
s-Pt(311)	1	2	86
	2	4	67
r-Pt(311)	1	3	88
	2	3	68

HAc is formed at Pt(311)

34

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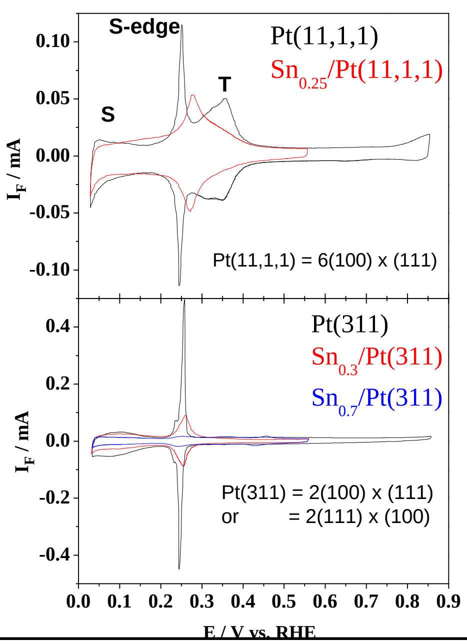

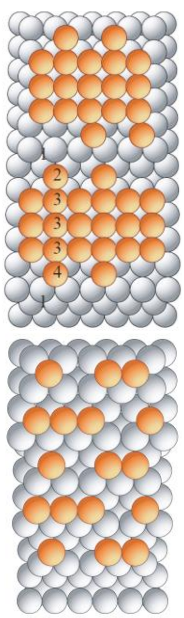

Sn atom is coordinated by 4-Pt atoms at terraces

-Only one type of site for Sn deposition
-Monoatomic rows

35

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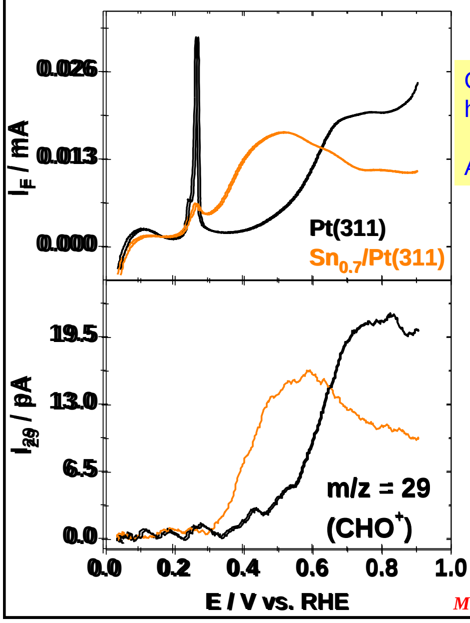
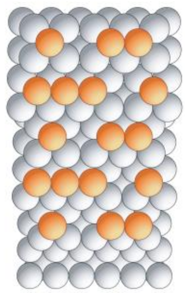
Ethanol Oxidation: Surface Modification with Sn



1. Cyclic voltammetry

Onset potential shifts negatively by 0.2 V, high ox. current at low potentials.

At E > 0.6: current decreases



-Only one type of site for Sn deposition

-Monoatomic rows

CO_2 formation?

Mostafa et al., Phys. Chem. Chem. Phys., 14:16115 (2012)

36

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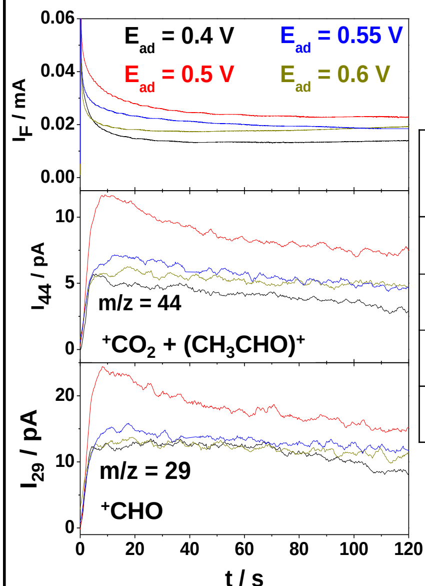
2. Potential step



CO_2 and Acetaldehyde Current Efficiencies on **$Sn_{0.7}$/Pt(311)**

E / V vs. RHE	$A_{44}^{CO_2}$ %	ϑ_{CO} %	A_{29}^{CHO} %
0.4	0	17	46
0.5	0	12	60
0.55	0	3	55
0.6	0	1	68

$$I_{44}^{(CH_3CHO)^+} = 0.55 \cdot I_{29}^{(^+CHO)}$$

A_{29} < 100 % : acetaldehyde and acetic acid are the main oxidation products

37

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- Introduction
- Different types of DEMS cells
- Application of DEMS
- Ex.1: MeOH (oxidation, mechanism, kinetic, catalyst effect and ads. rate)
- Ex.2: Effect of surface structure on the electrooxidation of ethanol
- Ex.3: ORR and OER in aprotic electrolyte
- Conclusions

38

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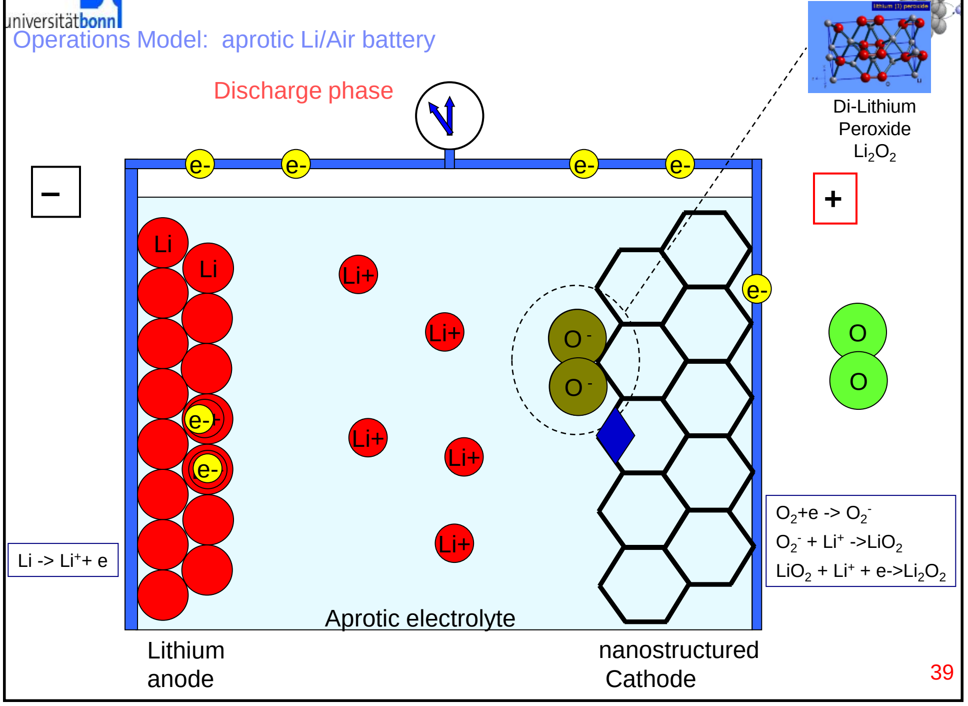
Operations Model: aprotic Li/Air battery



39

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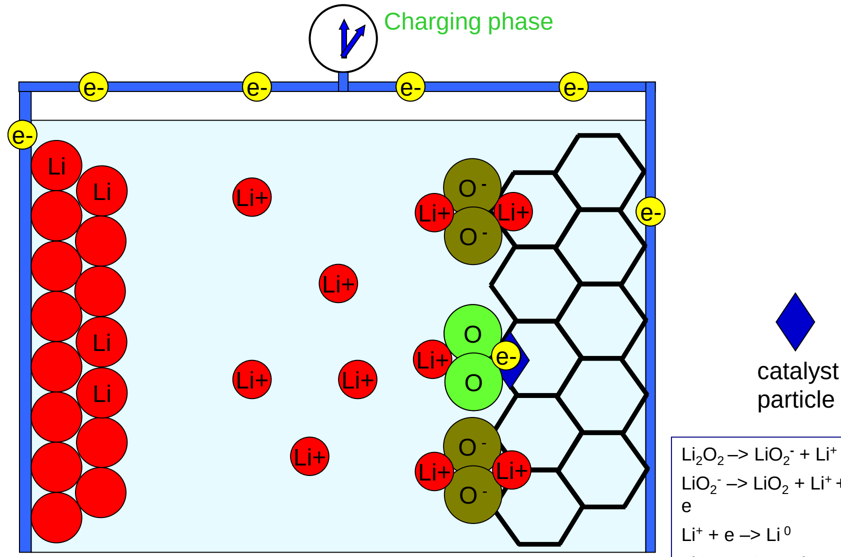
Operations Model: aprotic Li/Air battery



Li_2O_2 –> LiO_2^- + Li^+
LiO_2^- –> LiO_2 + Li^+ + e
Li^+ + e –> Li^0
LiO_2 –> O_2 + Li^+ + e
Li^+ + e –> Li^0

40

40

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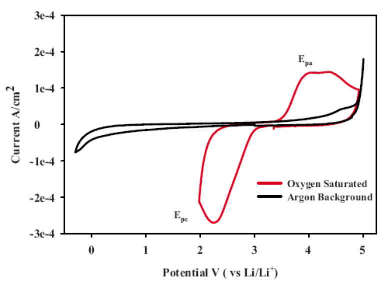
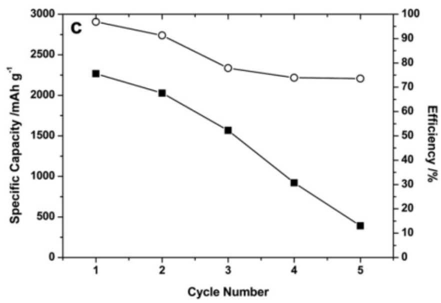
Apparent Coulombic Eff. From CV





$LiPF_6$-TG:Q_a/Q_c = 95%

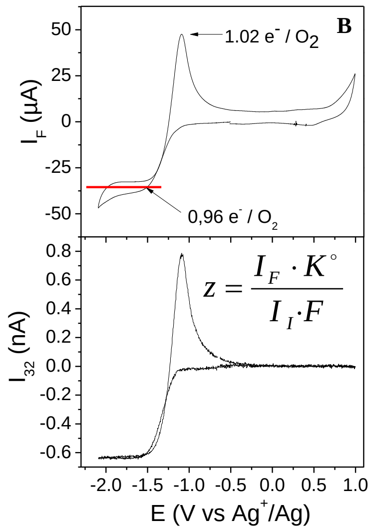
$LiClO_4$-NMP:Q_a/Q_c = 97%

Laoire et al., JECS 158(2011)A302

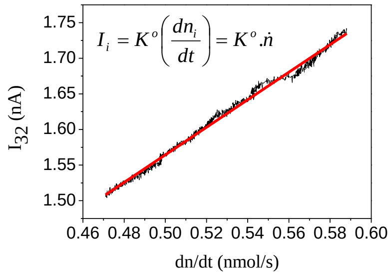
Wang at al., J power Sources 219(2012)263

41

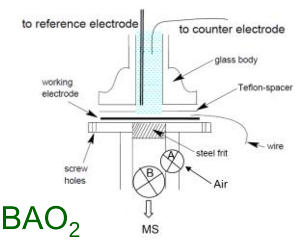
Calibration leak



$$z = \frac{I_F \cdot K^\circ}{I_I \cdot F}$$



$$I_i = K^o \left(\frac{dn_i}{dt}\right) = K^o.\dot{n}$$

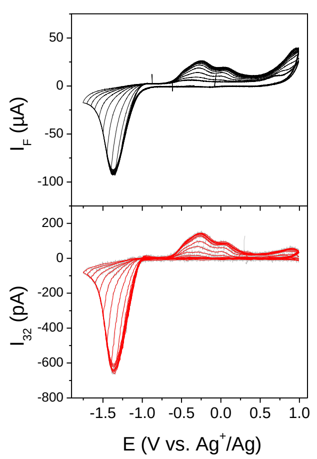


ORR: $O_2 + TBA^+ + e^- \rightarrow TBAO_2$

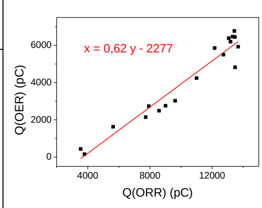
OER: $TBAO_2 \rightarrow O_2 + TBA^+ + e^-$

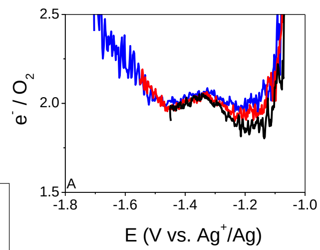
42

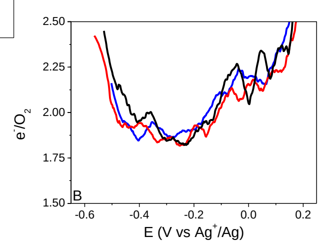
True Coulombic Eff. By DEMS



$$z = \frac{I_F \cdot K^\circ}{I_I \cdot F}$$







$LiClO_4$-DMSO:Q_a/Q_c = 60%

z_a and z_c~2 electron =>Li_2O_2 formation/oxidation

Laoire et al., JECS 162(2015)A487

43

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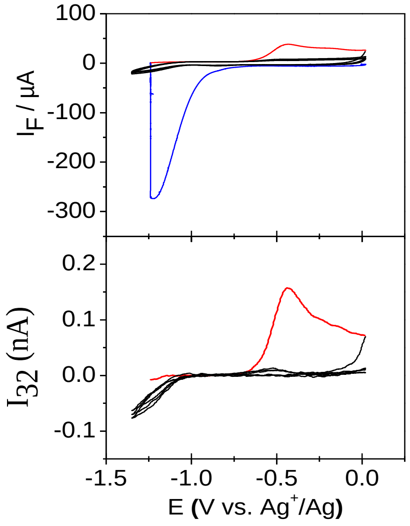
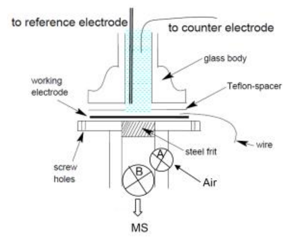
GDE





44

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Conclusions

- DEMS applications in qual. and quant. Analysis:
- Adsorbates characterization (coverage, adsorb. Rate and oxidation rate)
- Current Eff. of Faradaic reactions.
- ORR and OER in aq. or non-aq. Electrolytes
- Reactions mechanisms

  - Methylformate is directly formed during methanol oxidation at the Pt surface.
  - A_{44} is independent of the electrolyte flow rate ➔ parallel pathways.
  - At Pt_{poly}, Pt(11,1,1) and Pt(19,1,1): The main product of ethanol oxidation is CH_3CHO. A_{29} ≈ 100%
  - (111) sites very active for HAc formation
  - True Col. Eff. For OER/ORR is 60% in Li^+-DMSO, z = 2

Outlook

- Improve the construction of new DEMS cell.
- Detection of soluble products by ESI-MS.

45

Thank you for your kind attention

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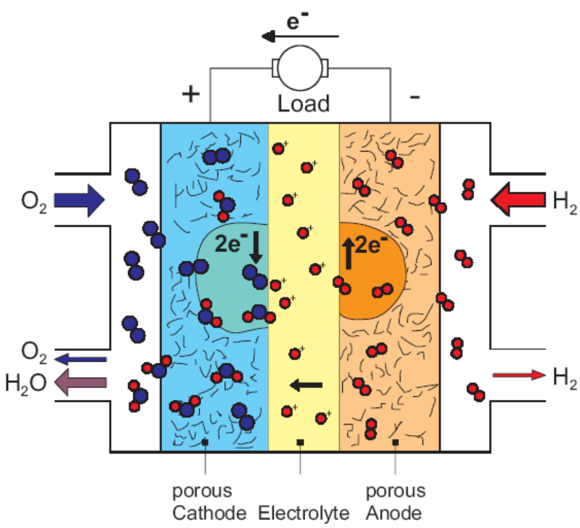
Motivation and aim of the work

Fuel cell



H_2 disadvantage: Clean production, storage and transportation

Alternative: MeOH and EtOH

47

Carrette et al., Fuel Cells **1**(2001)5.