Catalysts for the Oxygen-Reduction Reaction in PEMFCs

Nina Travitsky

Tel-Aviv University

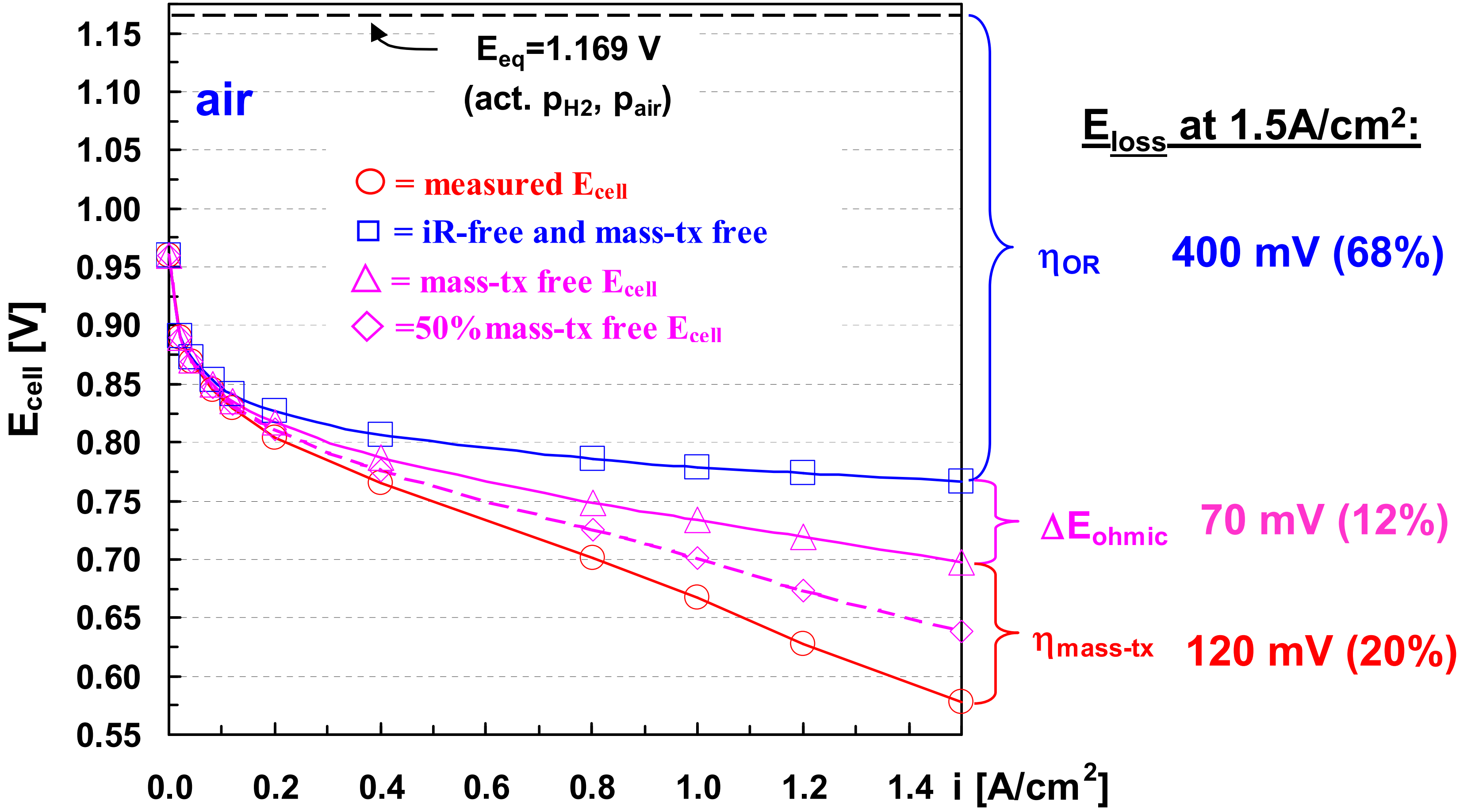
IFCBC Meeting, December 24, 2006

Outline

- Introduction
- Catalyst preparation
- Catalyst characterization
- ORR activity measurements
- Catalyst poisoning by MeOH, EG and their oxidation by-products

Voltage Losses in State-of-the-Art H_2/O_2 Fuel Cells

From: M.K. Carpenter et. al., ACS Meeting, September 10-14, 2006



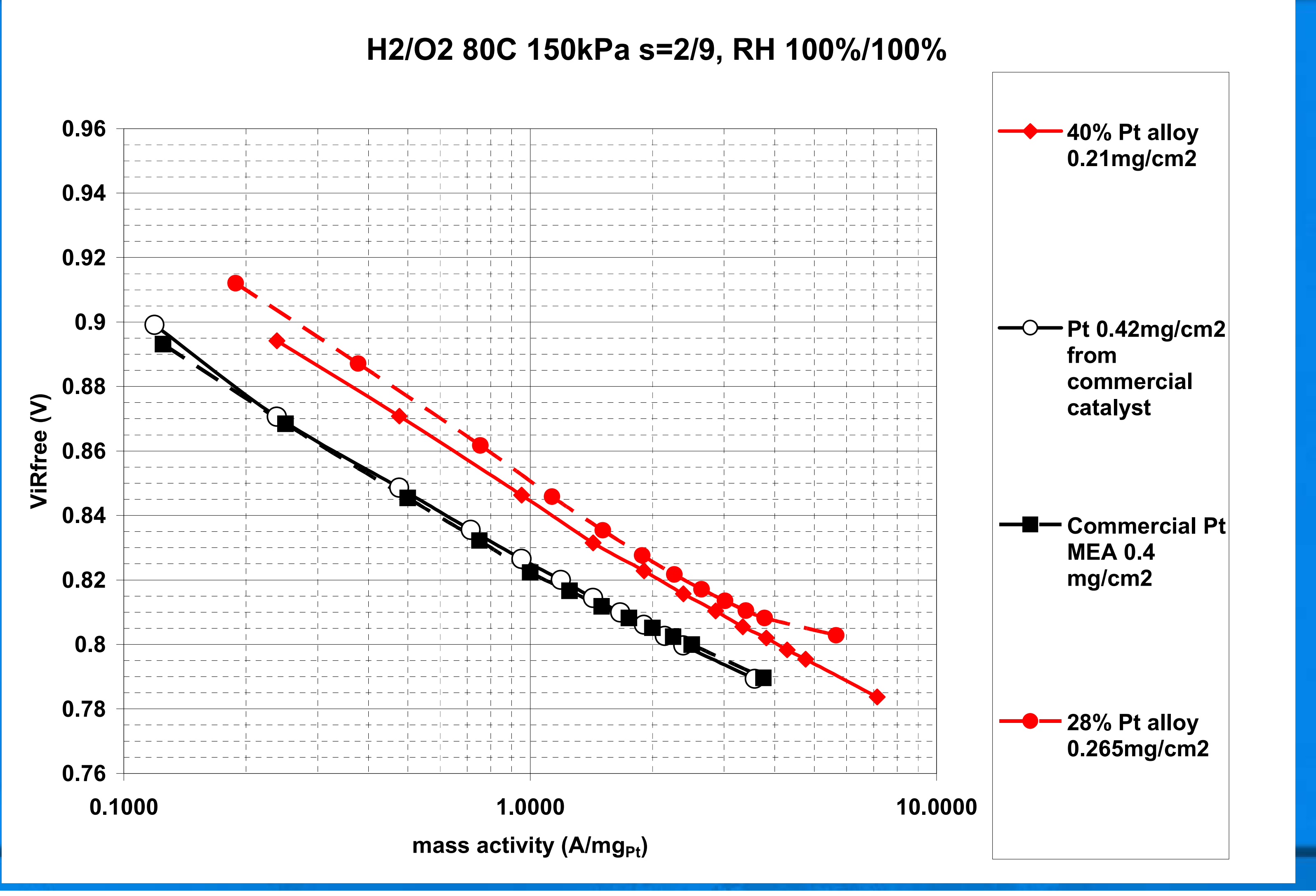
- major losses due to poor cathode kinetics (ORR)
- minor losses by ohmic resistance
- gains through improved flowfields/diffusion media (mass-tx)

Cathodic overpotential

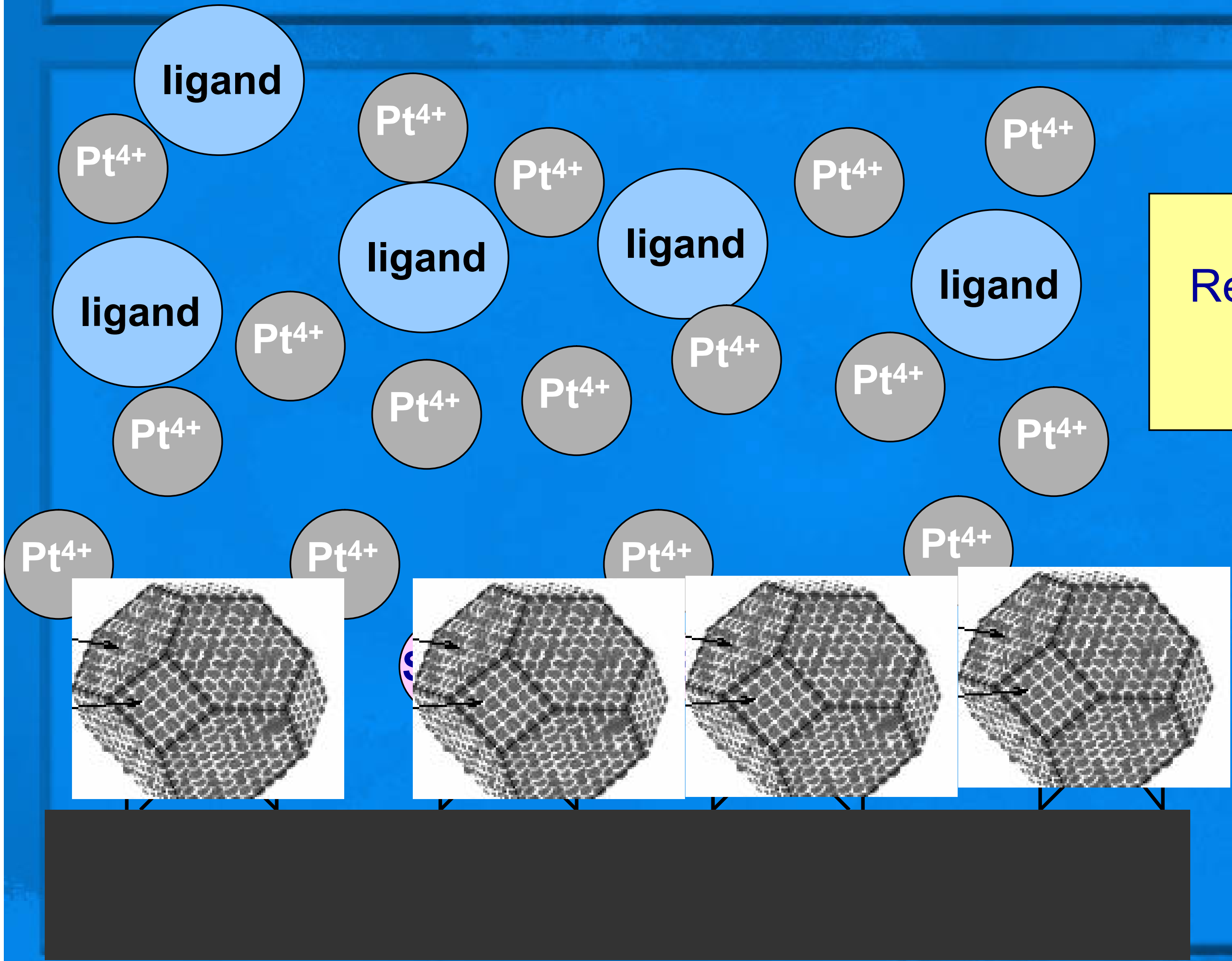
- 4e$^-$ reaction competing with 2e$^-$ reaction
- Poisoning effect of OH^- adsorbed species
- Poisoning effect of various anions
- Electrochemical surface-area loss
- Dissolution of Pt (also Pt-O site exchange)
- Fuel poisoning due to crossover

Why Pt alloys? Higher mass activities in PEM H_2 fuel cells

From: M.K. Carpenter et. al., ACS Meeting, September 10-14, 2006



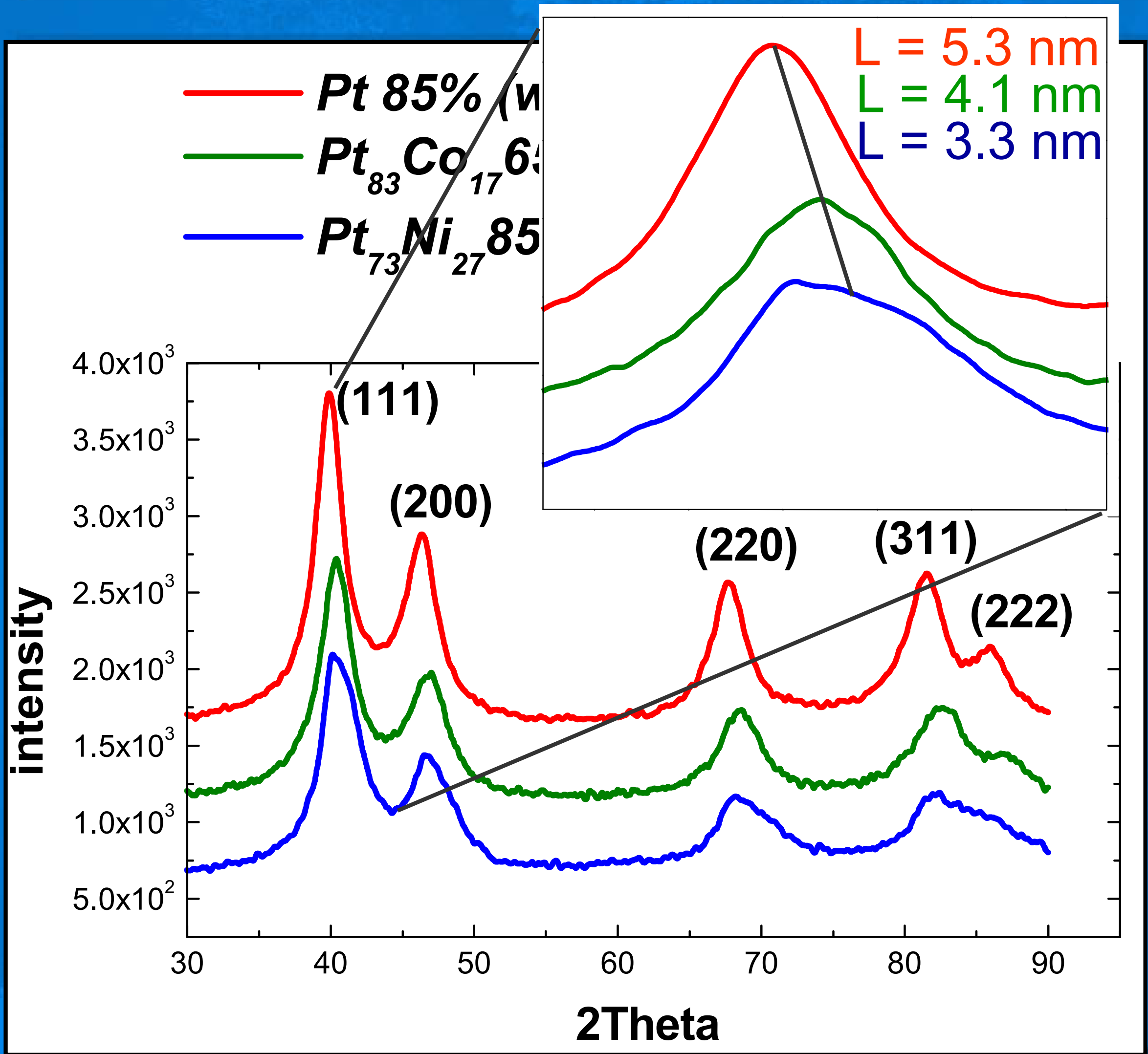
Preparation method - schematic



Reducing agent – $NaBH_4$

R : -OH, =O, -OOH

Alloying effect on grain size and lattice parameter



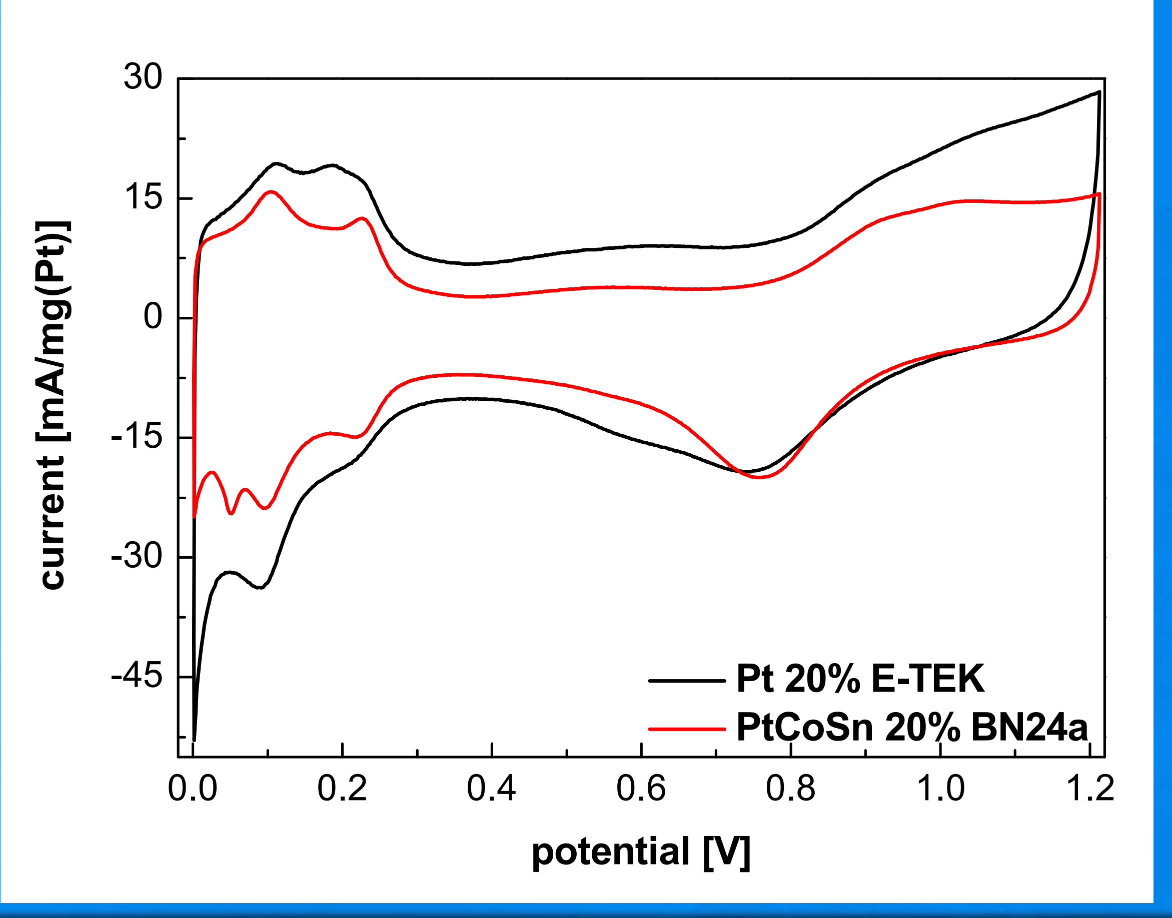
- Grain size:

$$L = \frac{0.92\lambda}{\beta \cos\theta}$$

- Alloy composition by lattice parameter:
a_0 (Pt) = 3.9231 Å
a_0 (Co) = 3.5447 Å
a_0 (Ni) = 3.5238 Å

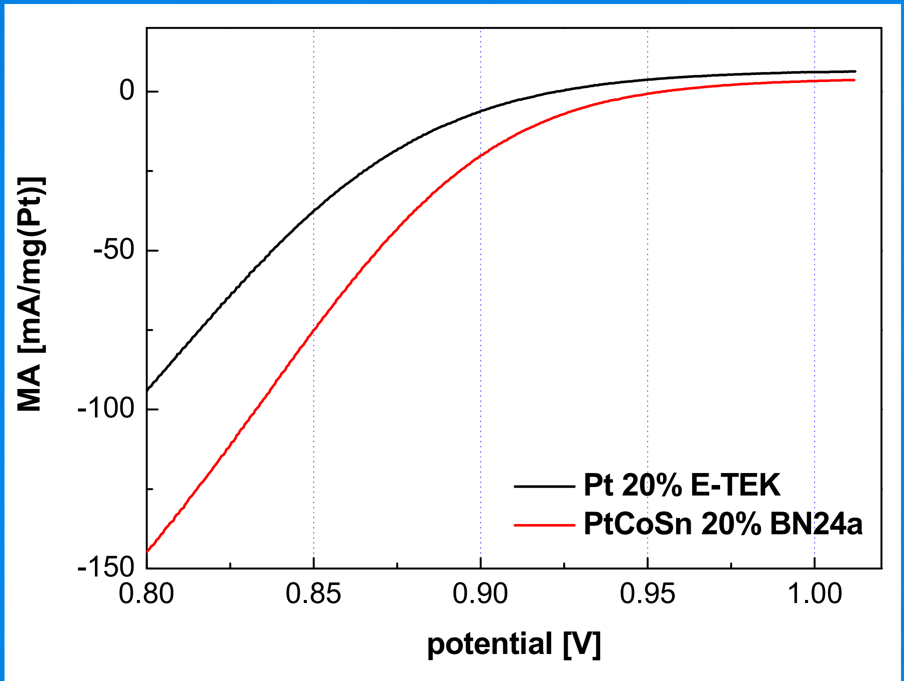
Alloying effect on CV shape and ECSA

Commercial and homemade

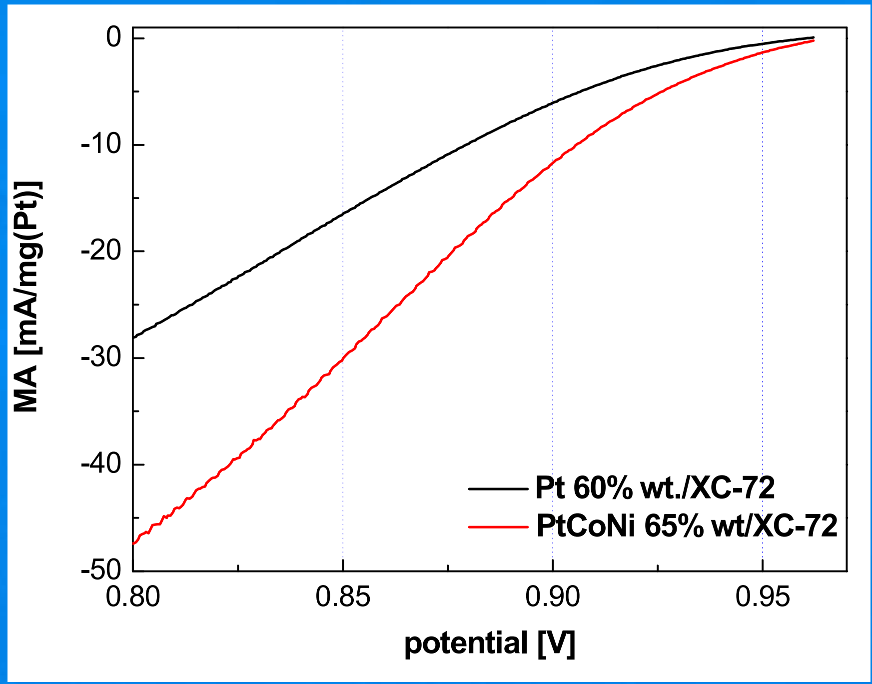


Alloying effect on ORR activity

Commercial and homemade



Homemade



Pt skin formation

Catalyst	Treatment	Composition		
		EDS	XPS	XPS after sputtering
PtCo (65%wt.)/XC72 homemade	-	$Pt_{48}Co_{52}$	$Pt_{37}Co_{63}$	$Pt_{42}Co_{58}$
	15h H_2SO_4 1M, 80°C	$Pt_{79}Co_{21}$	$Pt_{96}Co_4$	$Pt_{82}Co_{18}$
PtCo (20%wt.)/XC72 commercial	-	$Pt_{48}Co_{52}$	$Pt_{45}Co_{55}$	-
	20h H_2SO_4 1M, 80°C	$Pt_{80}Co_{20}$	$Pt_{100}Co_0$	$Pt_{83}Co_{17}$

Similar results were obtained for PtNi homemade catalyst

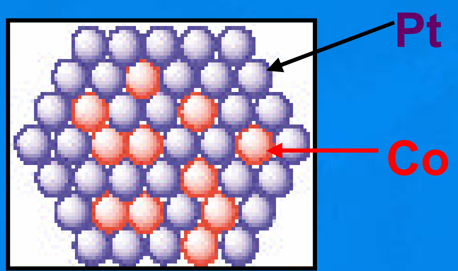
Alloy catalysts - conclusions

Experimental observations:

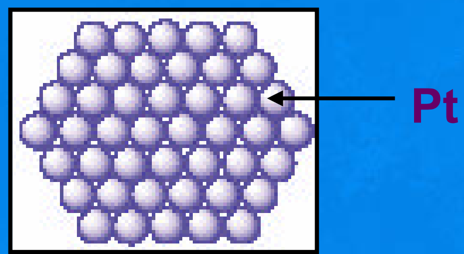
- ✓ Corrosion of PtNi / PtCo alloys levels off at ~ $Pt_{70}Ni_{30}$ and ~ $Pt_{80\text{-}85}Co_{20\text{-}15}$ composition.
- ✓ Catalyst particle surface is enriched in platinum relative to the bulk - 96% Pt *vs* 79% (this work Pt-Co catalyst), 100% Pt *vs*. 80% (commercial).

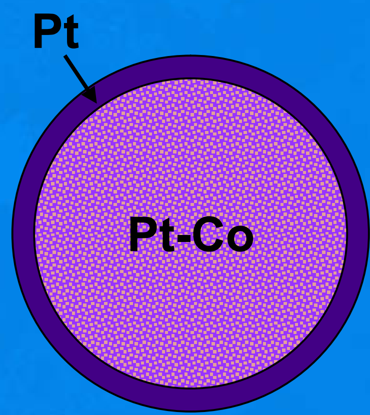
Explanation: Ni/Co corrodes from surface leaving a pure or almost pure skin of Pt which stops further corrosion.

Before treatment



After treatment



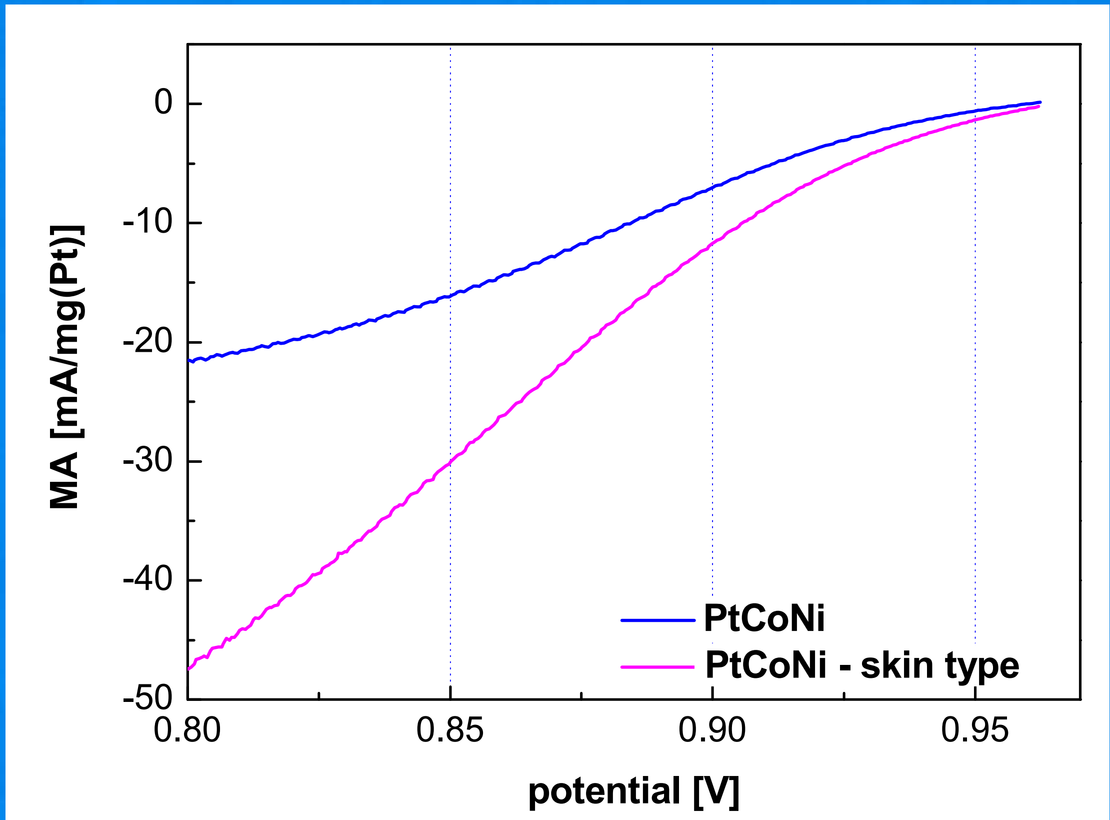


Top view

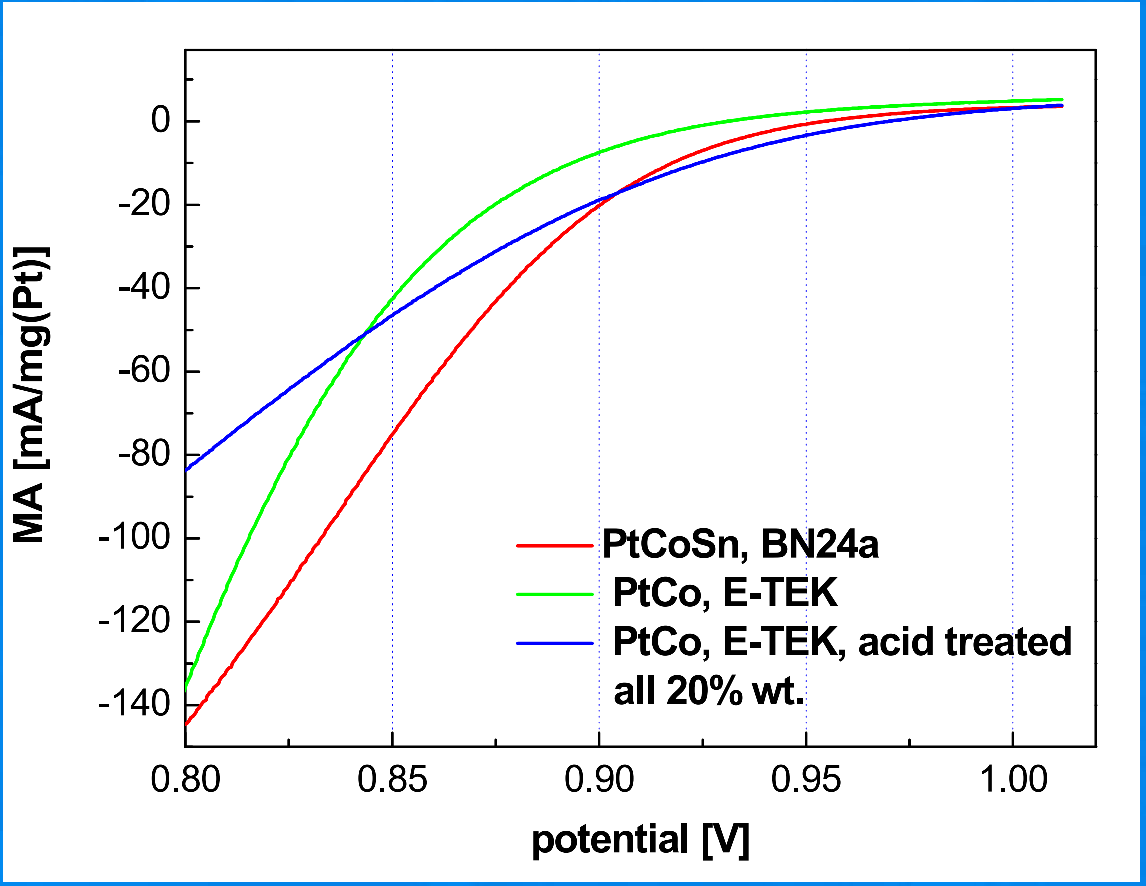
Side

Conclusion: The ideal catalyst structure - Pt skin is obtained

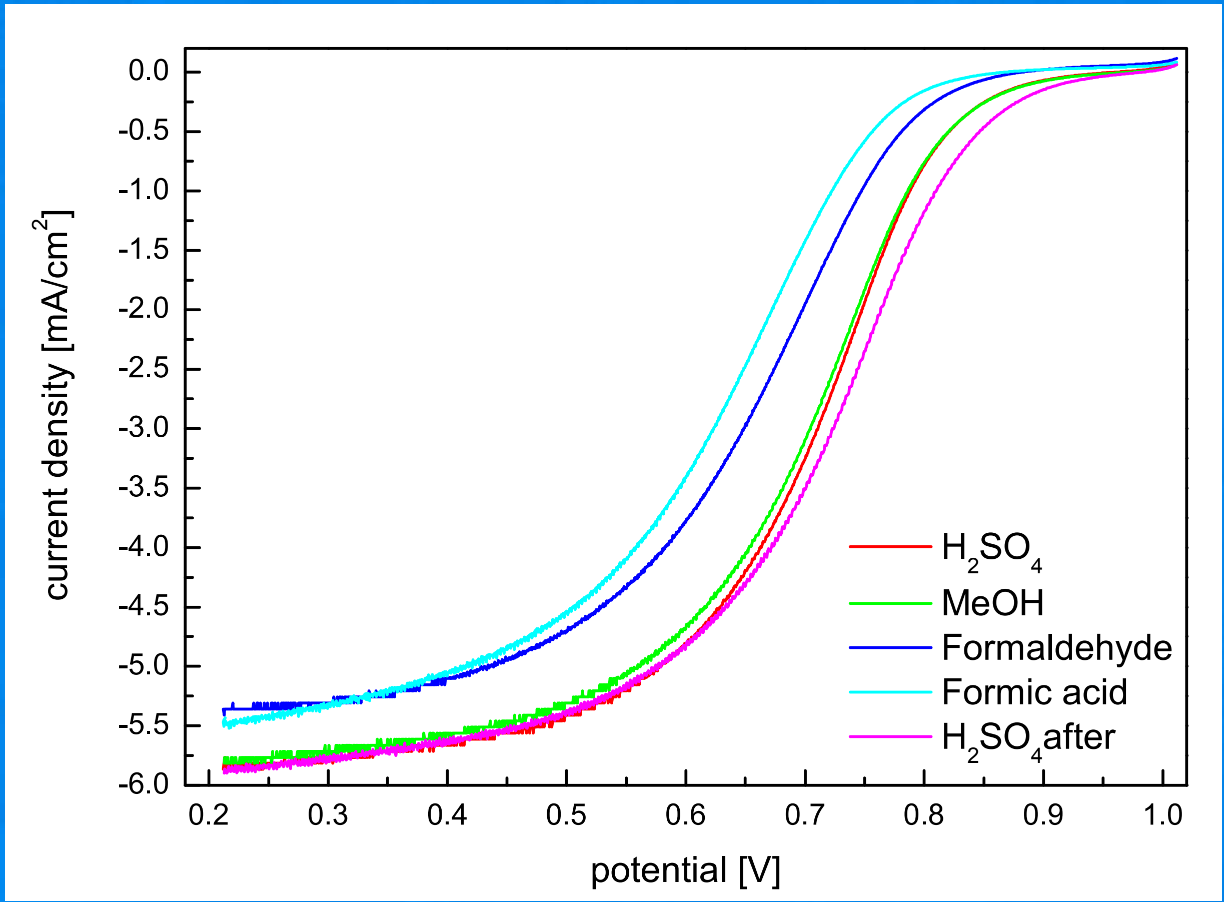
Skin effect on ORR activity - RDE tests



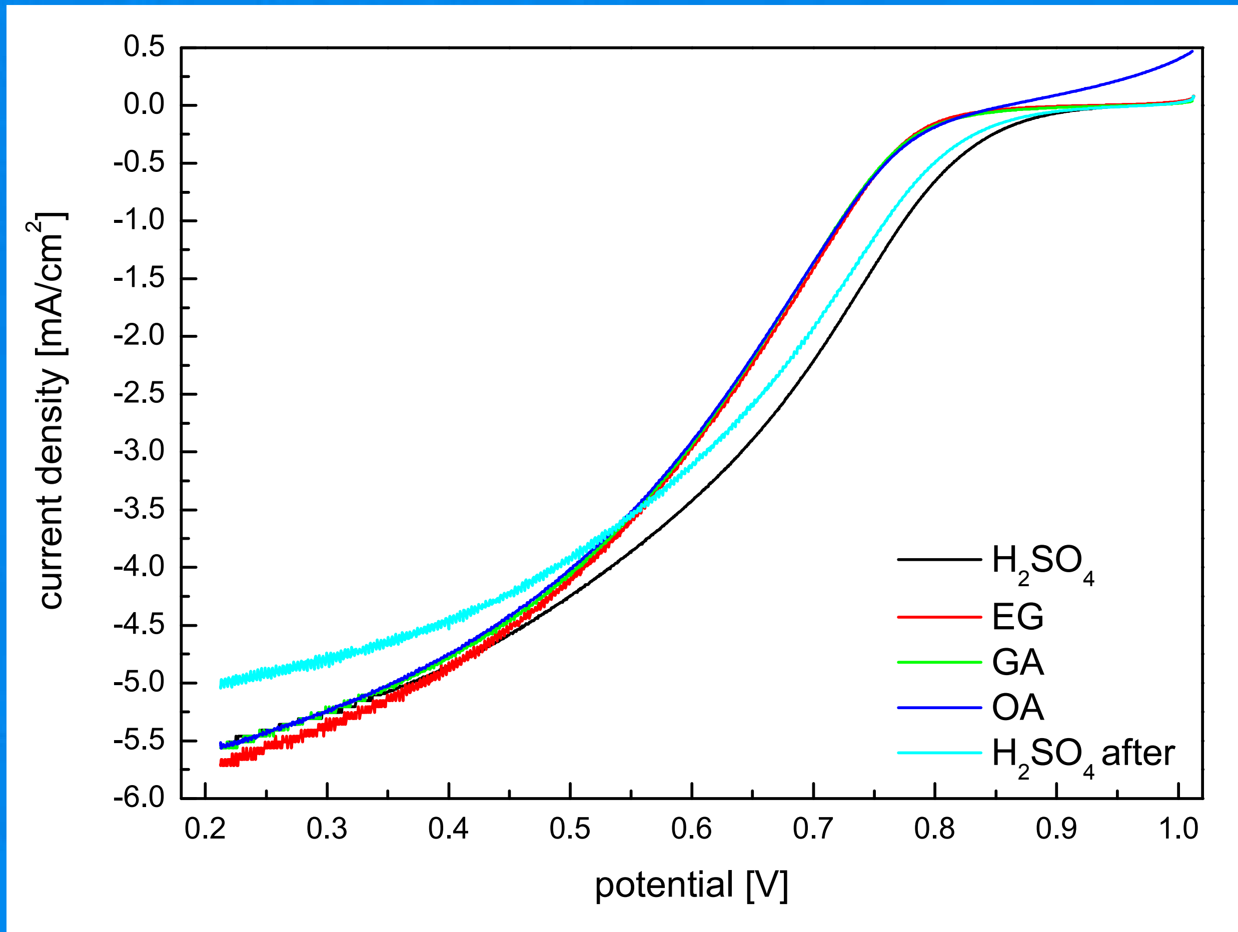
Synthesized catalysts *vs* commercial – RDE tests



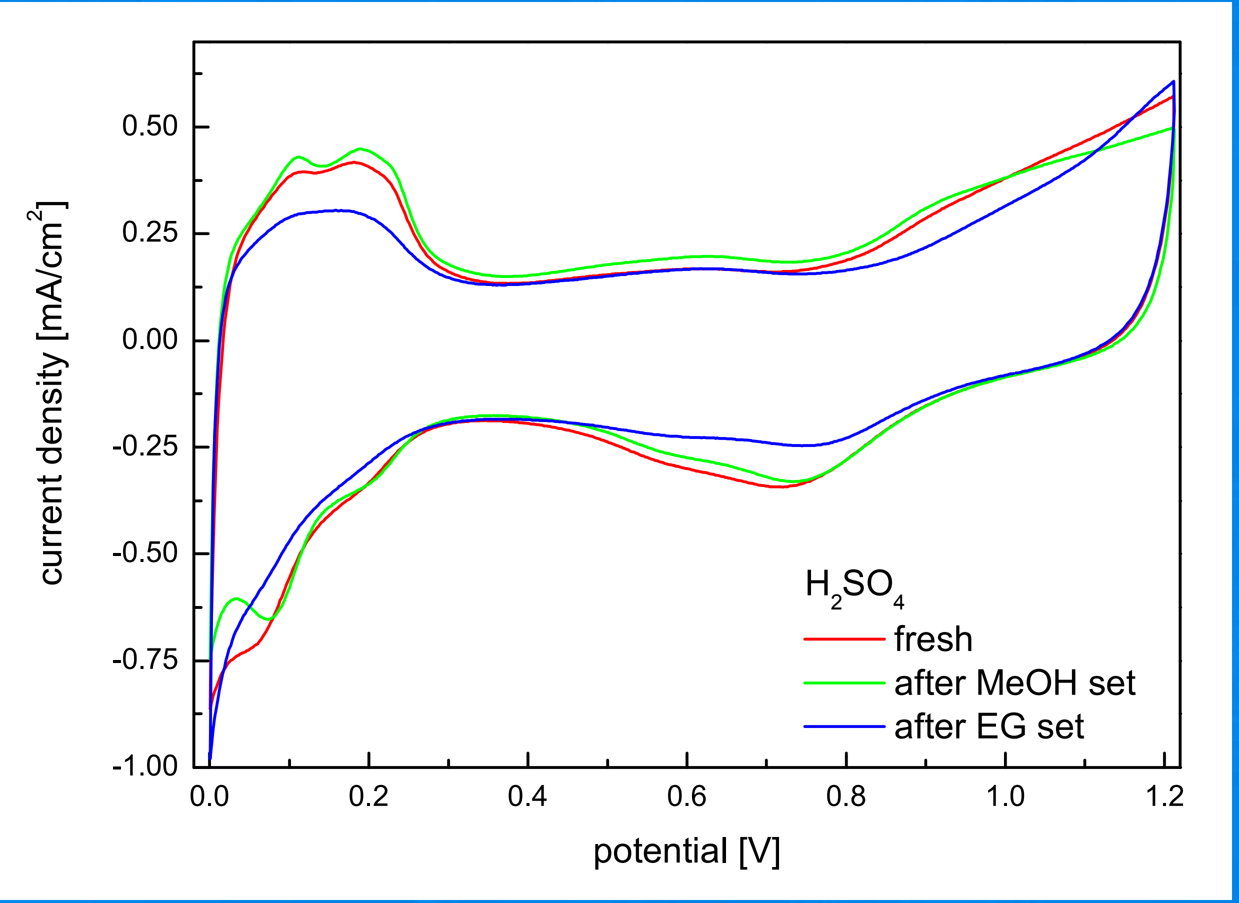
MeOH effect on Pt catalyst activity



EG effect on Pt catalyst activity



Fuel effect on Pt ECSA

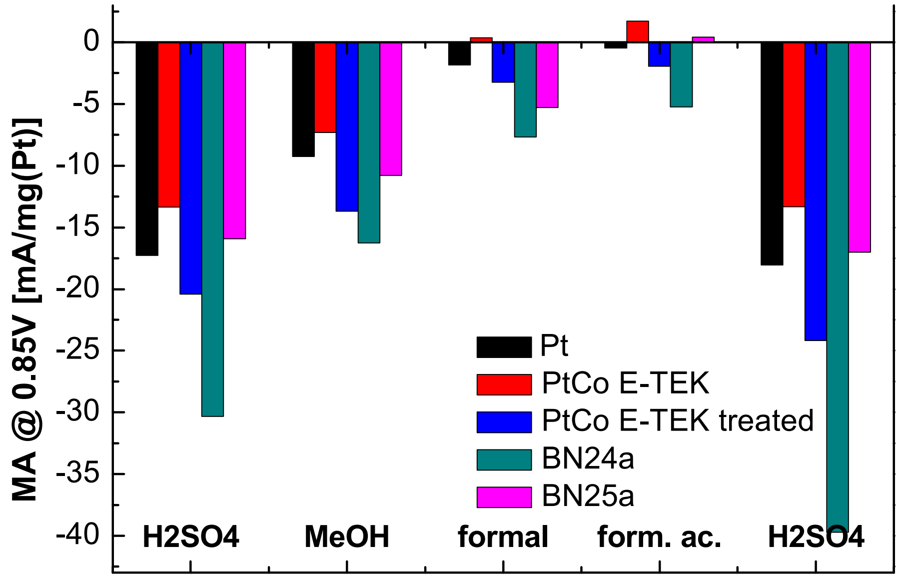


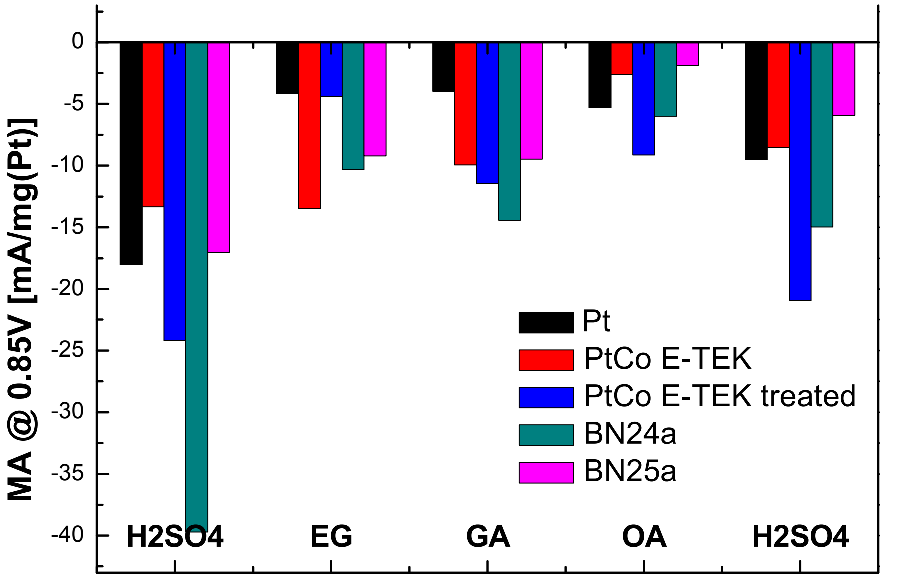
Catalyst properties

	Pt E-TEK	PtCo E-TEK	PtCo E-TEK treated	PtCoSn BN24a	PtCoNi BN25a
Grain size [nm]	2.3	3.2	3.1	2.6	2.5
ECSA [m^2/g]	93	81	62	66	61
Surface composition (by XPS)	Pt	$Pt_{45}Co_{55}$	$Pt_{100}Co_0$	$Pt_{74}Co_0Sn_{26}$	$Pt_{100}Co_0Ni_0$
Bulk composition (by XPS after sputtering)	Pt	-	$Pt_{83}Co_{17}$	$Pt_{78}Co_{10}Sn_{12}$	$Pt_{86}Co_3Ni_{11}$

Graphic representation of fuel-poisoning effect

MA @ 0.85 V





Fuel-poisoning reversibility

MeOH, EG and their oxidation intermediates - effect on ECSA

	Pt E-TEK	PtCo E-TEK	PtCo E-TEK treated	PtCoSn BN24a	PtCoNi BN25a
Fresh H_2SO_4	93	84	62	66	61
After MeOH set	84	61	56	64	62
After EG set	67	68	39	63	49

Fuel poisoning - conclusions

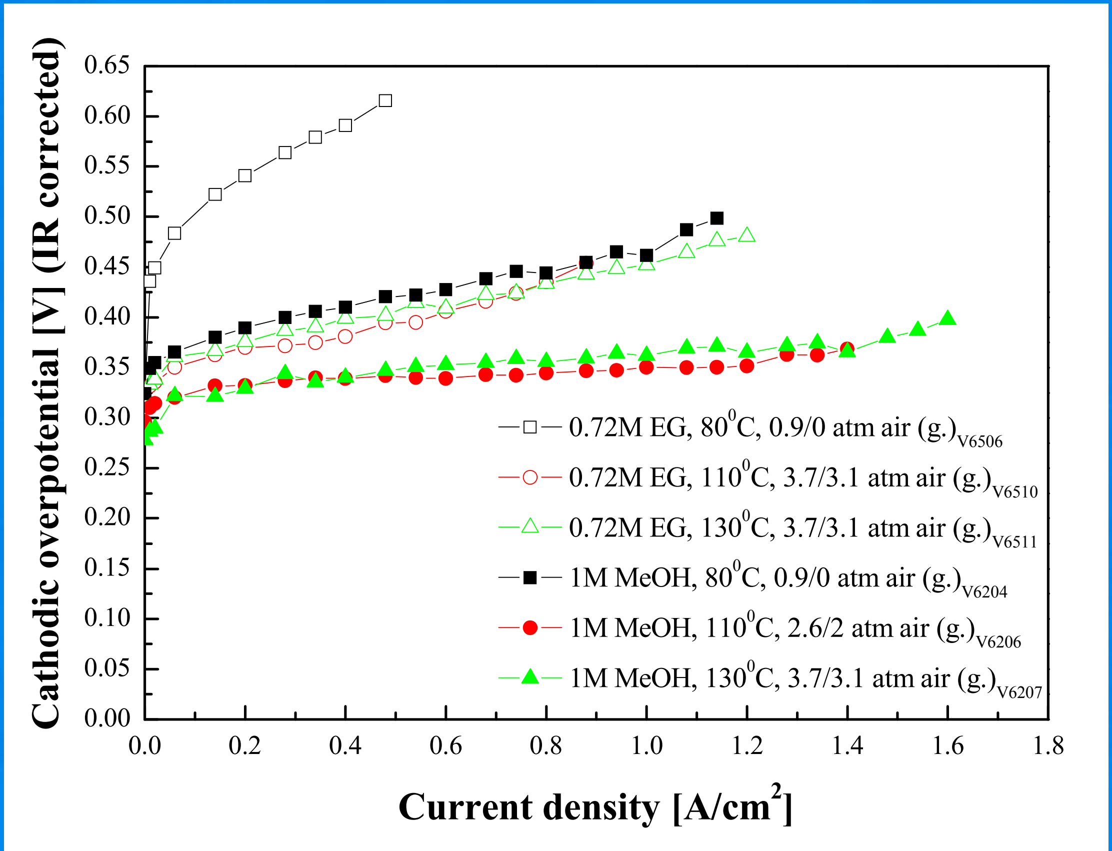
- The severity of poisoning is:

  MeOH < formaldehyde < formic acid

  EG ≤ GA < OA
- The most stable catalysts both in MeOH and EG poisoning are commercial acid-treated $Pt_{83}Co_{17}$ (surface composition: $Pt_{100}Co_{0}$) and homemade $Pt_{78}Co_{10}Sn_{12}$ (surface composition: $Pt_{74}Co_{0}Sn_{26}$).
- Poisoning effect of MeOH and its derivatives is reversible.
- Poisoning effect of EG and its derivatives is less reversible at room temperature.

Fuel poisoning - conclusions

DOFC polarization: MeOH *vs* EG



V. Livshits, E. Peled, *J. Power Sources, 161,* 2006, *1187*

Summary

- A new procedure for catalyst preparation was employed.
- Alloying with Co and Ni reduced grain size by 50% and 60% respectively.
- ORR activity of PtCoNi 60%(wt) catalyst was higher by 80% than that of Pt 60%(wt) powder.
- Corrosion of alloy catalysts was investigated. Corrosion of Co and Ni occurs on the surface of catalyst particles to produce Pt "skin".
- PtCoSn catalyst was found to be more active than PtCo commercial catalyst in ORR.
- Important conclusions were drawn regarding fuel poisoning.