

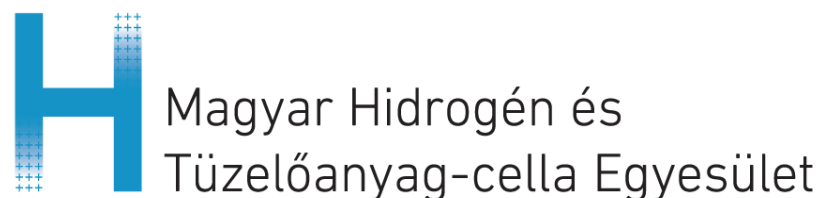


Magyar Hidrogén és  
Tüzelőanyag-cella Egyesület

## **Az MTA TTK kutatási tevékenységei és eredményei: elektrokatalizátorok, MEA -k**

**Tompos András**  
**MTA Természettudományi Kutatóközpont**  
**Anyag- és Környezetkémiai Intézet**

Budapest, 2013. május 7.



# **Activity and achievements at the Hungarian Academy of Sciences: electro-catalysts and MEAs**

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**Institute of Materials and Environmental Chemistry**  
**Research Centre for Natural Sciences**  
**Hungarian Academy of Sciences**

Budapest, May 7, 2013.

## Mission of Institute of Materials and Environmental Chemistry

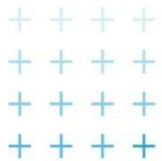
- Perform research on the chemical problems of materials science and environmental science.
- Research in materials science is aiming at revealing the chemical relationships among the composition, microstructure, properties and processing of selected structural and functional materials.
  - Development of micro- and nanosized materials/electrocatalysts
- Research in environmental chemistry is dedicated to disclose basic chemical and physicochemical phenomena in order to decrease the environmental impacts of products and technologies and to develop new processes and technologies with a minimum or negligible environmental impact.
  - Explore processes important in energy storage and transformation.





## **Institute of Materials and Environmental Chemistry in numbers**

- Number of co-workers: 124
- Number of researchers: 90
  - Below age of 35: 26
- Yearly budget
  - 2012 fact: 3 576 thousand €
  - 2013 plan: 3 551 thousand €
- Financial support from HAS
  - 2012 fact: 1 978 thousand €
  - 2013 plan: 1 528 thousand €



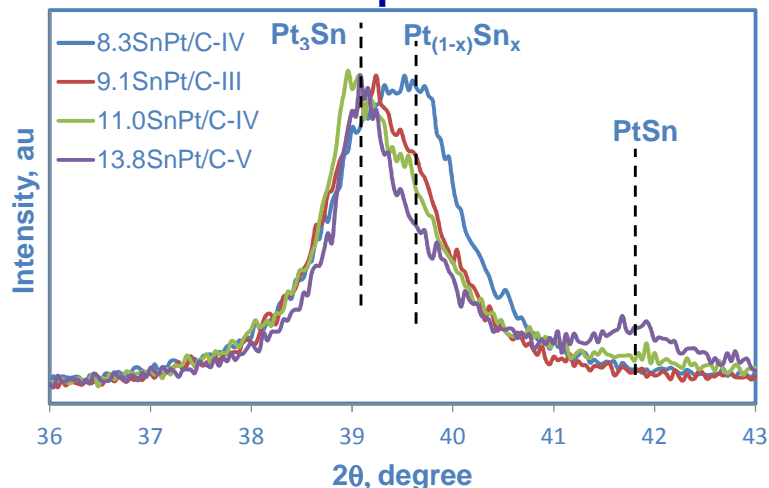
## Anode electrocatalysts (SnPt/C systems)

- Synthesis of a pure phase, selectively.  
Preparation of Pt<sub>3</sub>Sn alloy.
- Preparation by means of Controlled Surface Reactions (CSRs):
  - Formation of Primary Surface Complexes (step I)  
$$\text{Pt-H}_a + \text{Sn}(\text{C}_2\text{H}_5)_4 \rightarrow \text{Pt-Sn}(\text{C}_2\text{H}_5)_{4-x} + x \text{C}_2\text{H}_6$$
  - Decomposition of Primary Surface Complexes (step II):  
$$\text{Pt-Sn}(\text{C}_2\text{H}_5)_{4-x} + (4-x)/2 \text{H}_2 \rightarrow \text{Pt-Sn} + (4-x) \text{C}_2\text{H}_6$$



# Anode electrocatalysts (SnPt/C systems)

XRD patterns

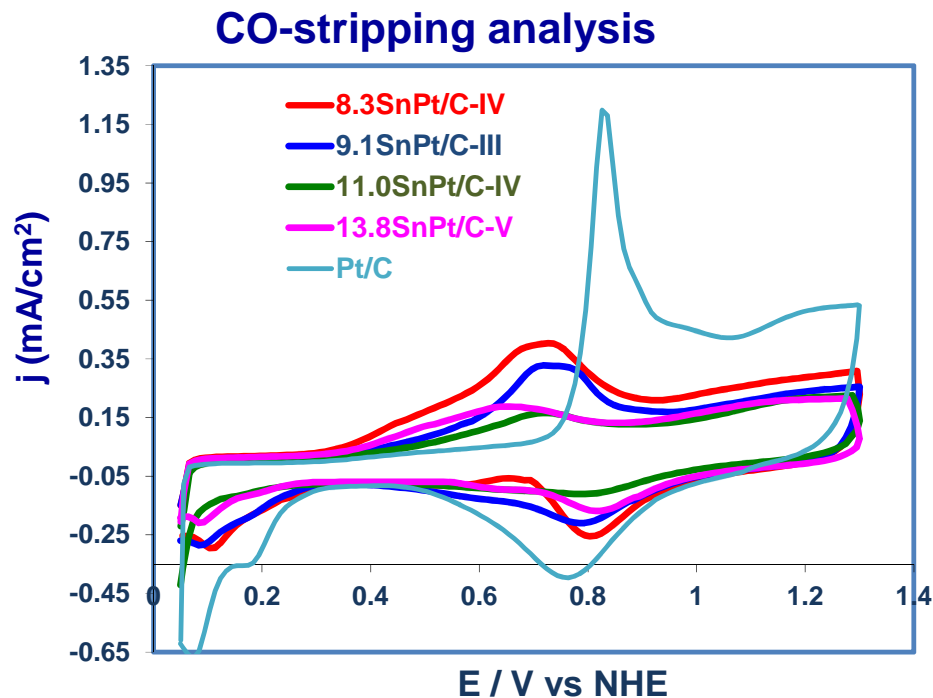


- With increasing tin content the particle size increases significantly.
- Appearance of PtSn alloy at higher tin content.

Samples	Pt/Sn at/at	Lattice parameter, Å (Phase, %)			Average particle size, nm		
		fcc Pt <sub>1-x</sub> Sn <sub>x</sub>	fcc Pt <sub>3</sub> Sn	hcp PtSn	Pt <sub>1-x</sub> Sn <sub>x</sub>	Pt <sub>3</sub> Sn	PtSn
<b>8.3SnPt/C-IV</b>	<b>2.9</b>	a: 3.933 (25%)	a: 3.975 (75%)	-	<b>8.3</b>	<b>8.3</b>	-
<b>9.1SnPt/C-III</b>	<b>2.7</b>	a: 3.933 (20%)	a: 3.985 (80%)	-	<b>9.1</b>	<b>10</b>	-
<b>11.0SnPt/C-IV</b>	<b>2.2</b>	a: 3.945 (35%)	a: 3.99 (60%)	(5%)	<b>5.8</b>	<b>12</b>	<b>5.8</b>
<b>13.8SnPt/C-V</b>	<b>1.8</b>	a: 3.945 (20%)	a: 3.99 (70%)	(10%)	<b>9.1</b>	<b>17</b>	<b>14</b>



## Anode electrocatalysts (SnPt/C systems)



- The presence of Sn promotes CO electrooxidation compared to Pt/C catalyst
- The onset potential is shifted to lower values.
- At low overpotentials the current density increases upon decreasing the tin content.
- At higher tin content appearance of PtSn 1:1 alloy and the higher particle size must be responsible for the decrease in the electrooxidation activity.

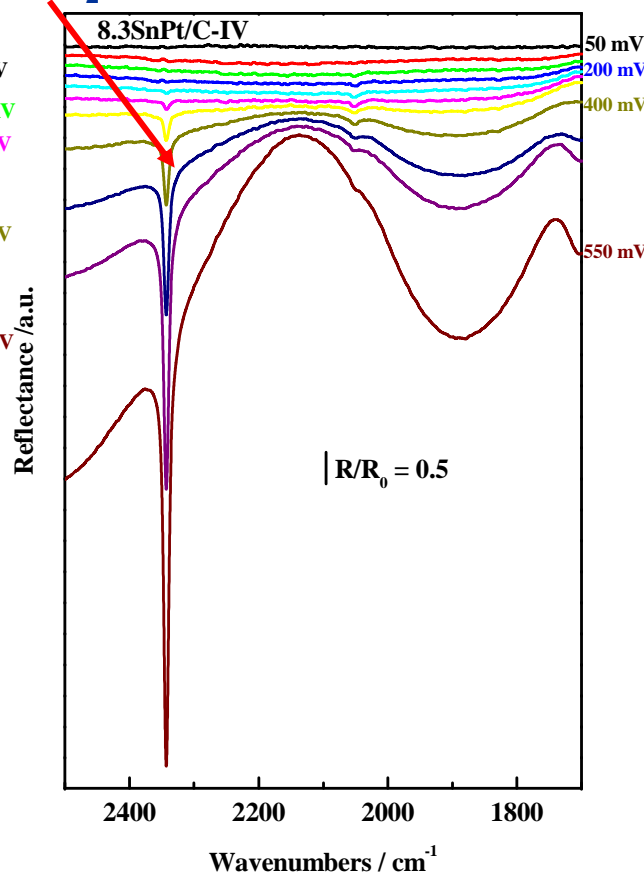
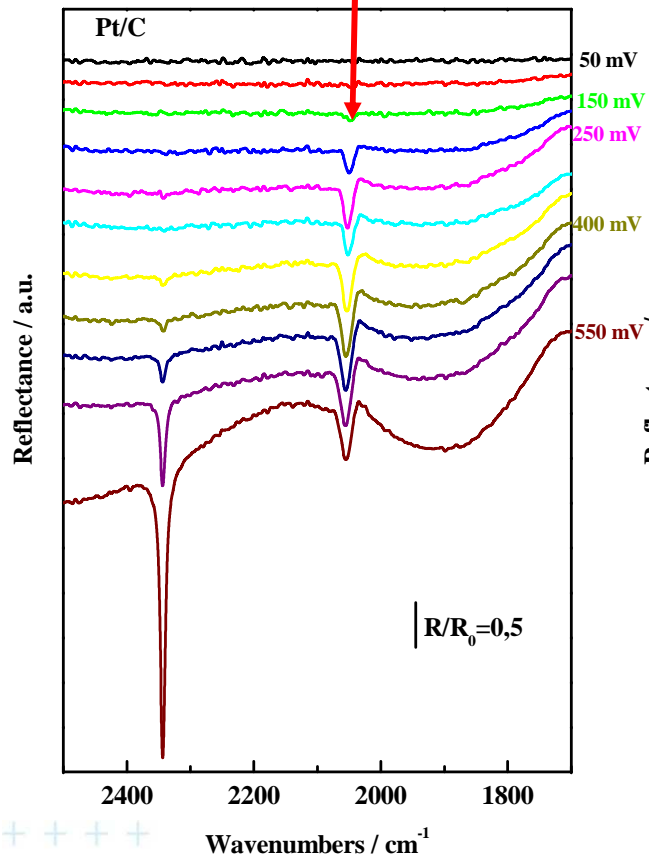


# Anode electrocatalysts (SnPt/C systems)

In situ FTIR of methanol electrooxidation

$\text{CO}_{\text{ad}}^-$  2050  $\text{cm}^{-1}$

$\text{CO}_2^-$  2343  $\text{cm}^{-1}$



- Tin has a strong dilution effect
- Decreased number of Pt ensembles prevents methanol dehydrogenation to CO
- Direct oxidation of methanol to  $\text{CO}_2$  is promoted over the Sn-modified electrodes





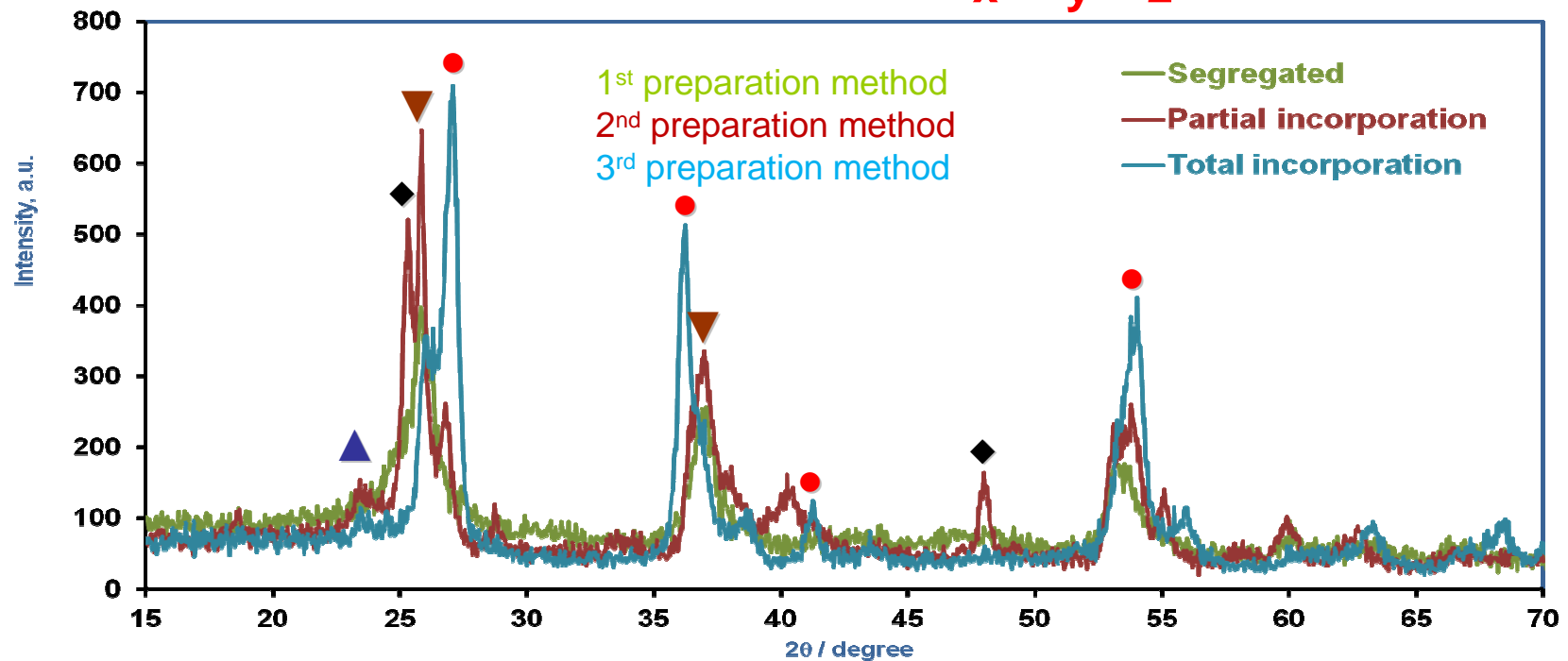


## Anode electrocatalysts ( $\text{Pt/Ti}_x\text{W}_y\text{O}_2\text{-C}$ systems)

- Synthesis of a pure phase, selectively. Composite of activated carbon and Ti-W-mixed oxides in rutile phase.
- Preparation methods used for perfect incorporation of  $\text{WO}_2$  into  $\text{TiO}_2$  rutile:
  - Sol-gel method followed by a short, low temperature treatment (2 h, 650 °C)
  - Sol-gel method followed by a higher temperature treatment with longer duration (8 h, 750 °C)
  - Formation of  $\text{TiO}_2$  rutile phase at RT by means of a new type of sol gel method followed by long heat treatment at high temperature (8 h, 750 °C)

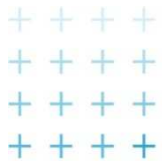


## Anode electrocatalysts (Pt/Ti<sub>x</sub>W<sub>y</sub>O<sub>2</sub>-C systems)

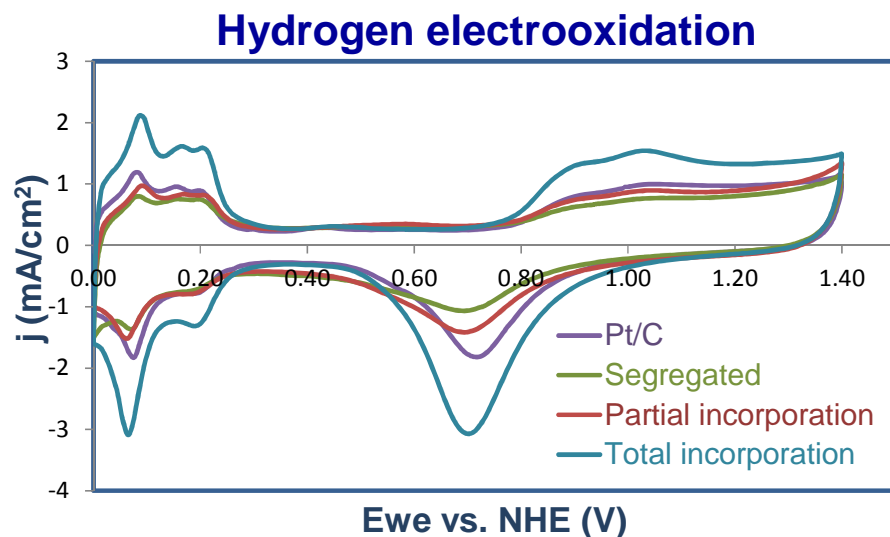


XRD pattern of Ti<sub>x</sub>W<sub>y</sub>O<sub>2</sub>/C samples prepared using various pathways of sol-gel-based multistep synthesis. ● Rutile, ◆ Anatase, ▲ WO<sub>3</sub>, ▼ WO<sub>2</sub>.

- Preliminary formation of a pure TiO<sub>2</sub> rutile has been proved to facilitate W incorporation.



## Anode electrocatalysts (Pt/Ti<sub>x</sub>W<sub>y</sub>O<sub>2</sub>-C systems)

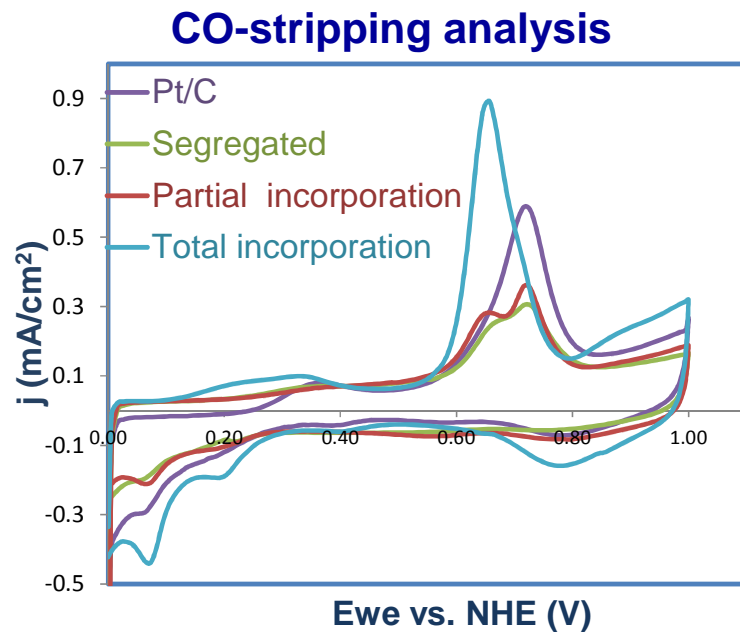


	ECSA (m <sup>2</sup> /g catalysts)	Pt SA (m <sup>2</sup> /g Pt)
Pt/C	15.1	37.7
Segregated	10.1	25.2
Partial incorporation	11.4	28.6
Total incorporation	18.8	47.0

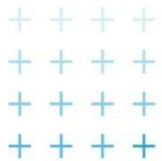
- The sample with total tungsten incorporation proved to have significantly higher active surface than the unmodified carbon supported Pt catalyst.



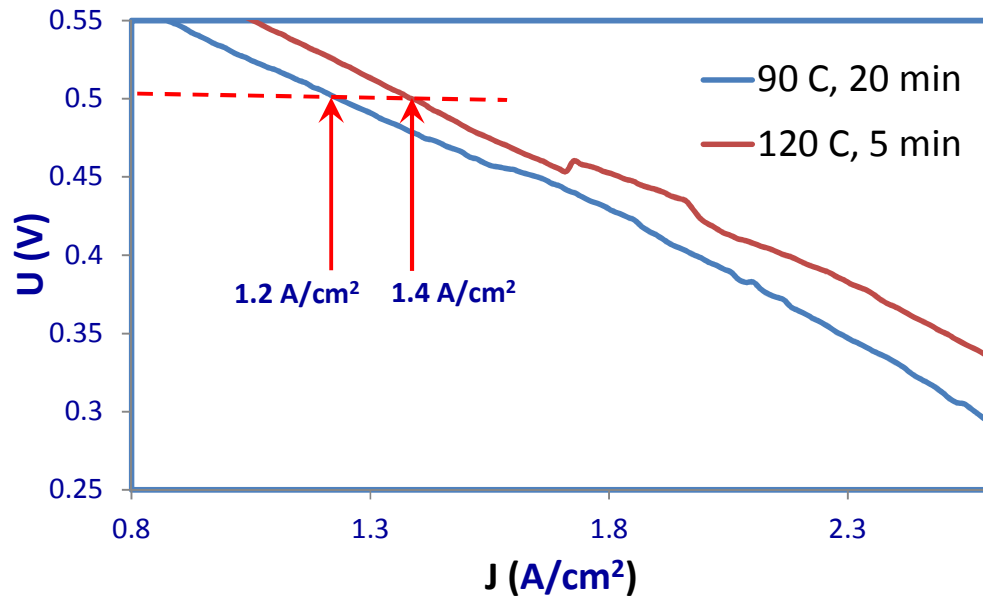
## Anode electrocatalysts ( $\text{Pt}/\text{Ti}_x\text{W}_y\text{O}_2\text{-C}$ systems)



- Composite sample with total tungsten incorporation had better CO tolerance than the Pt/C
- Two peaks is evident over the sample with smaller degree of W incorporation
  - The one at lower potentials characteristic to the sample with total tungsten incorporation
  - The peak at higher potentials can be attributed to Pt sites supported over composite without tungsten incorporation.



## Membrane electrode assemblies (MEAs)



- Condition of hot pressing of MEAs has been investigated
- A shorter treatment at a higher temperature seems to be advantageous.





## Ongoing projects and future plans

- Development of noble metal free cathode electrocatalyst based on carbon structures
- Development of novel bipolar plates based on electro conducting composites of polymers and carbons
- Proton conducting polymers
- Carbon based super-capacitors
- Application of high-throughput experimental tools to get fast achievements in the above research areas



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