Combined STXM and TEM *in situ* imaging for nanoparticles film growth analysis

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Problem

- How to observe reactions in liquid inside an electron microscope?

Solution

- A chamber, transparent for electrons, that could be placed inside the microscope.

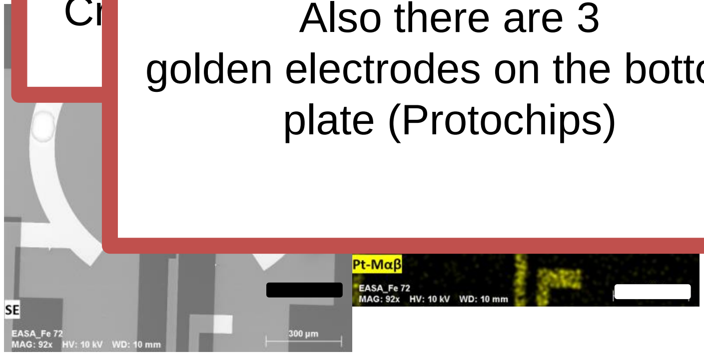
Transmission electron microscopy (TEM) allows to observe nanostructures with extremely high resolution (down to below 1 Å). But in order to analyse physical reactions *in situ*, a special technique is needed: Liquid Cell TEM. With this technique, we can perform experiments inside the TEM and image them in real time.

Liquid Cell
Transmission Electron Microscopy (LC-TEM)

Poseidon Select system for liquid cells. The bottom plate of the holder, a seal (the O-ring), the

E-chip for electrochemical experiments. Scale bar: 300 μm.

Also there are 3 golden electrodes on the bottom plate (Protochips)



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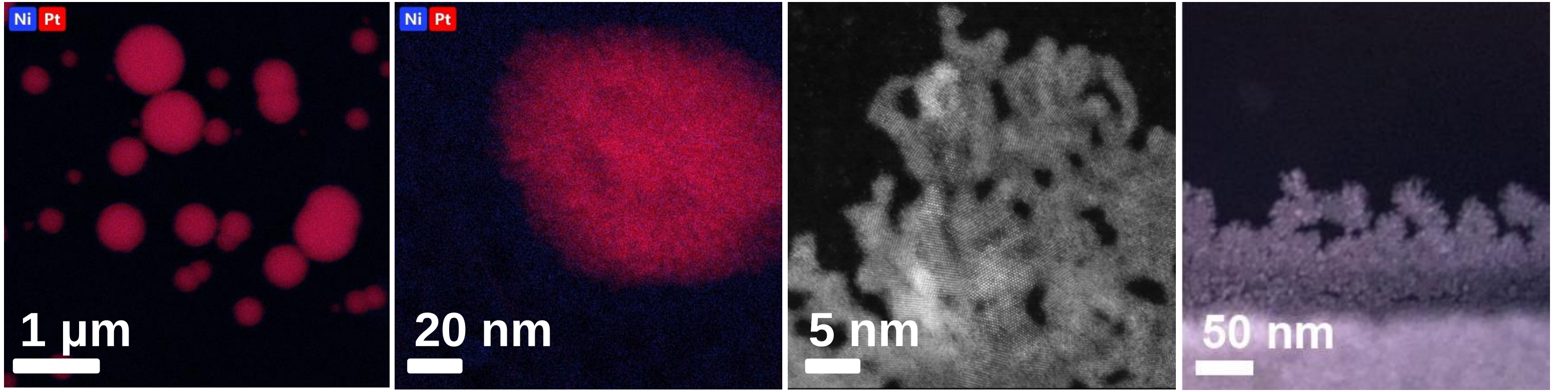
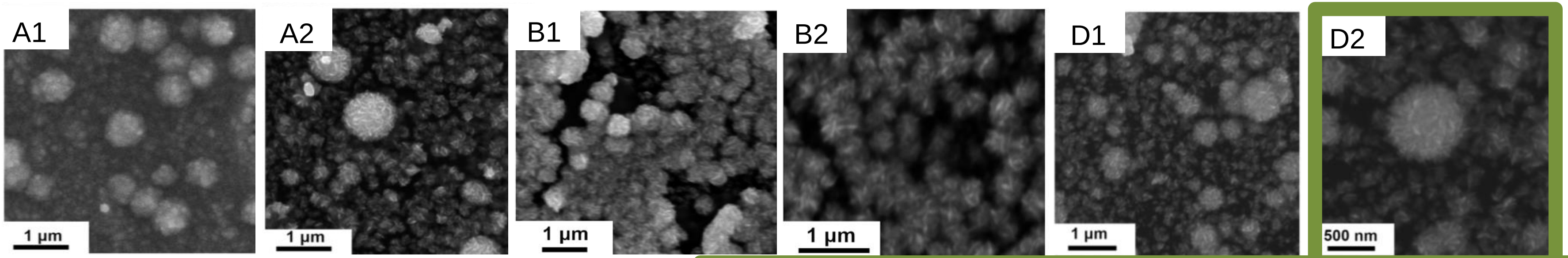
ELECTRODEPOSITION

Process

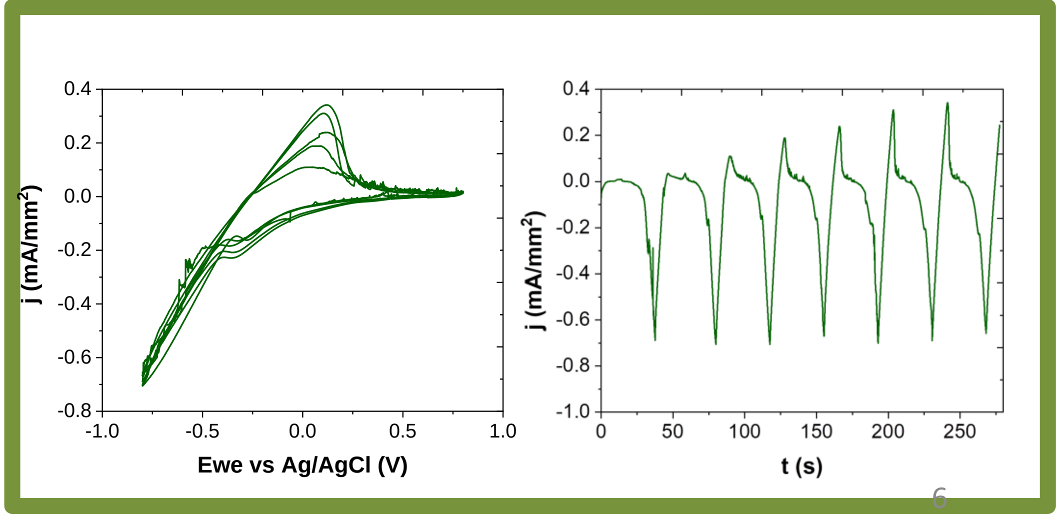
Real time observation of PtNi nanoparticle film growth via electrodeposition and understanding the growth mechanism.

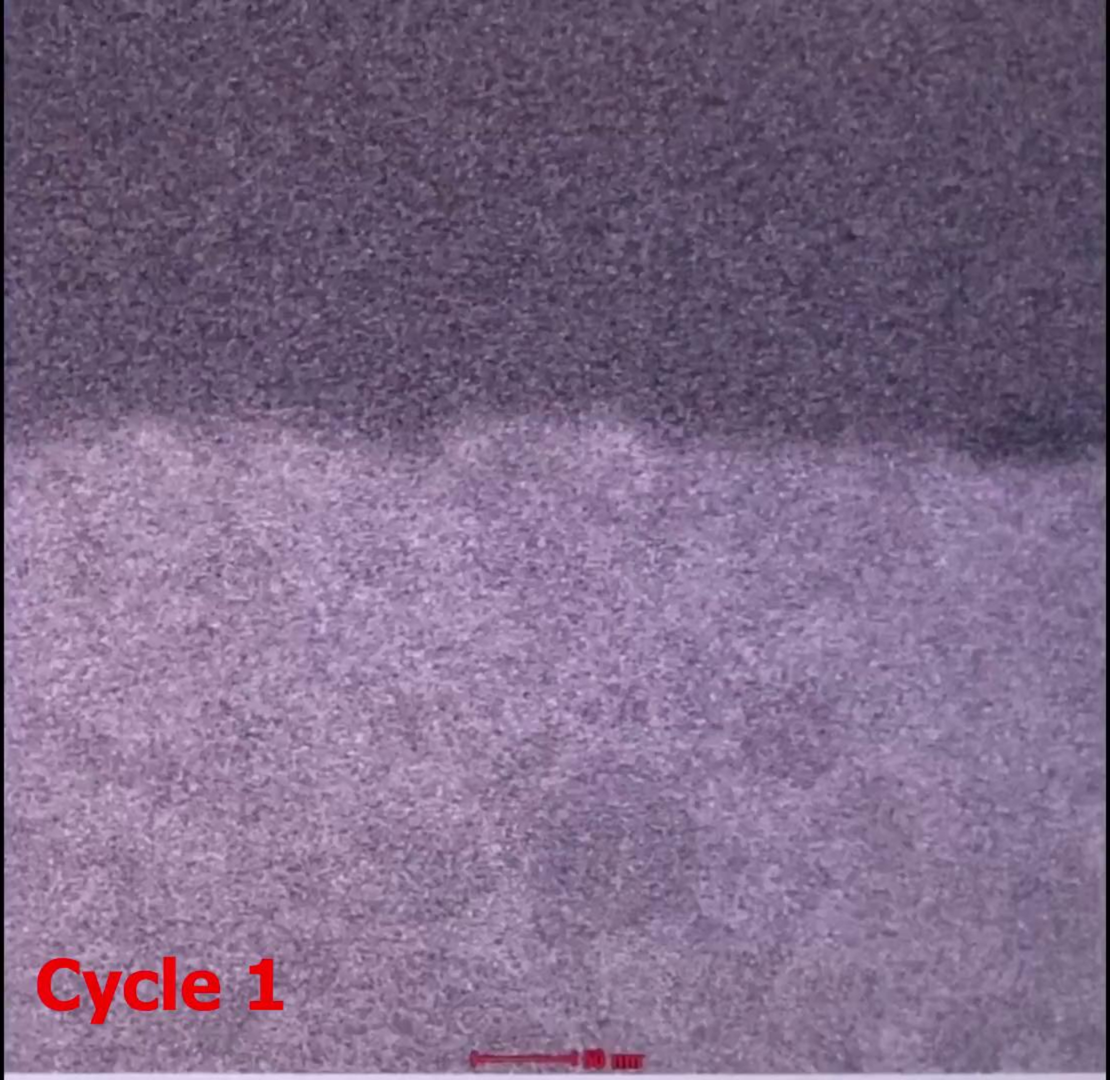


Choice of electrodeposition parameters



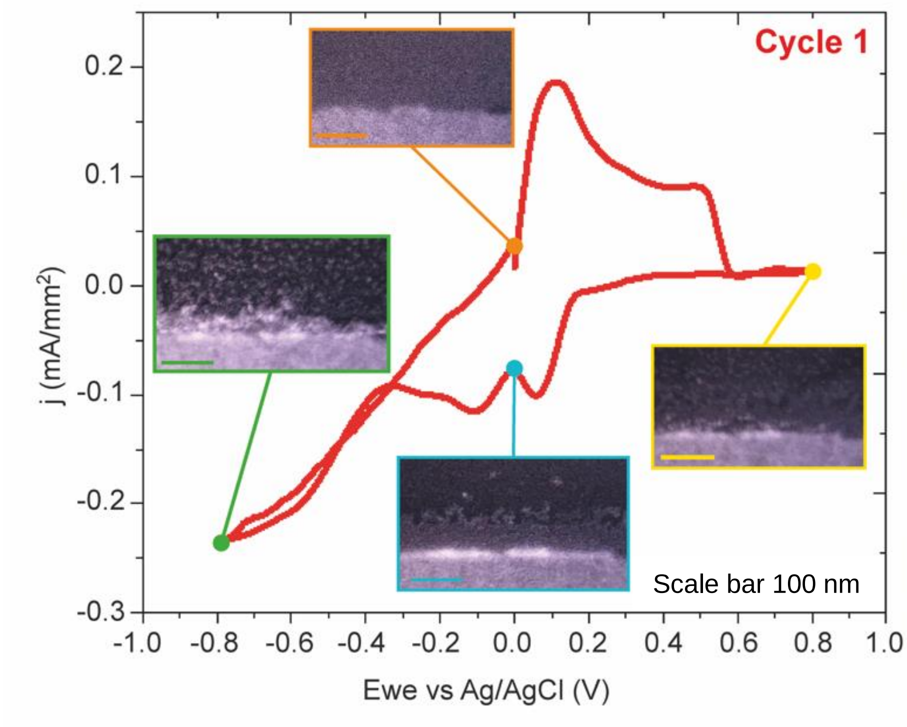
Parameter	Sample series					
	A1	A2	B1	B2	D1	D2
E_1 [V]	1.2		1.2		1.2	0.8
E_2 [V]	-0.8		-0.8		-0.8	-0.8
dE/dt [mV/s]	100		100	85	85	80
n	15	10	7		7	7

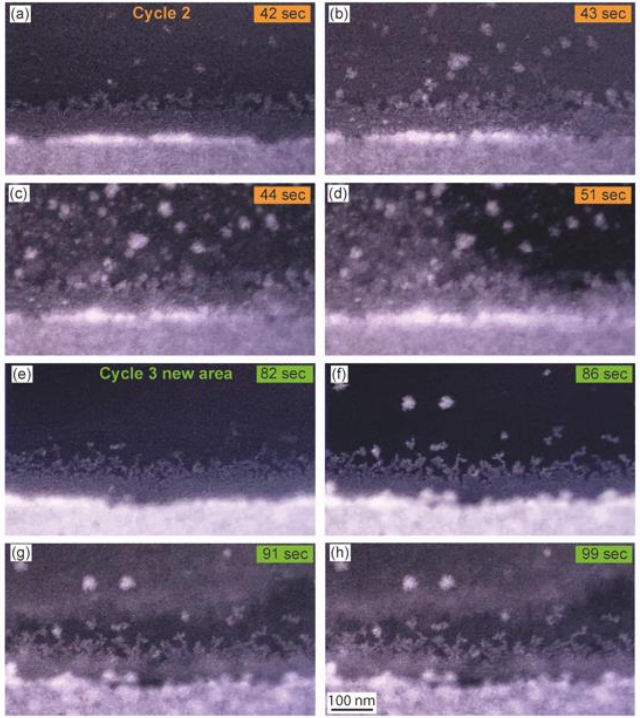



Cycle 1

Electrodeposition *in situ* Parameters and Results

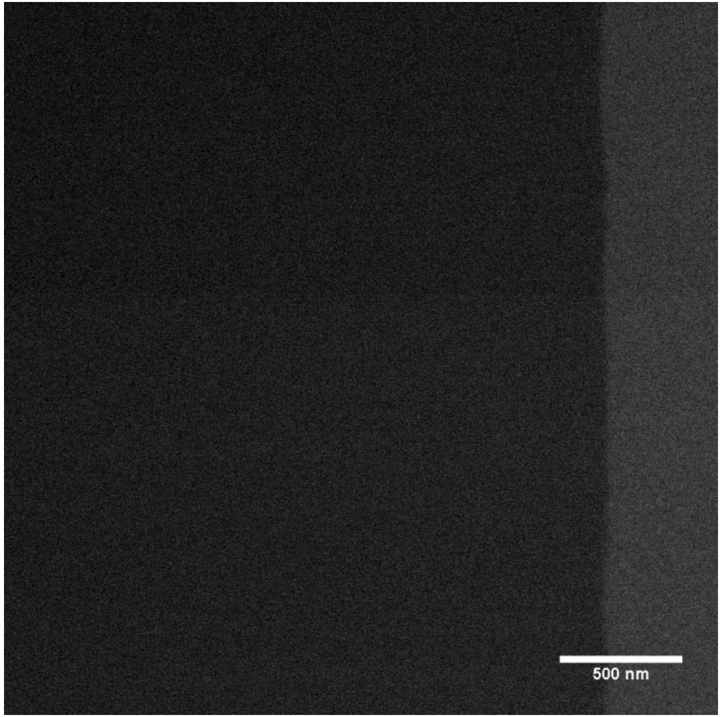
E_1 [V]	E_2 [V]	dE/dt [mV/s]	n	Electron Dose Rate [e/Å^{2}s]	Pump rate [µl/min]
0.8	-0.8	80	7	0.04	3





Electrodeposition *in situ* Lower scan rate

E_1 [V]	E_2 [V]	dE/dt [mV/s]	n	Electron Dose Rate [e/Å^{2}s]	Pump rate [µl/min]
0.8	-0.8	10	7	0.04	3

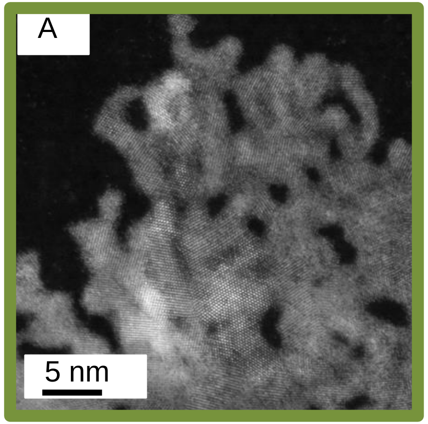


Another electrodeposition was performed for deeper investigation of the process. With lower scan rate and lower magnification, it becomes visible how the nanospheres nucleate and grow on the whole electrode and interconnect. After 2nd cycle, the stress inside the film is too high and the film detaches from the electrode.

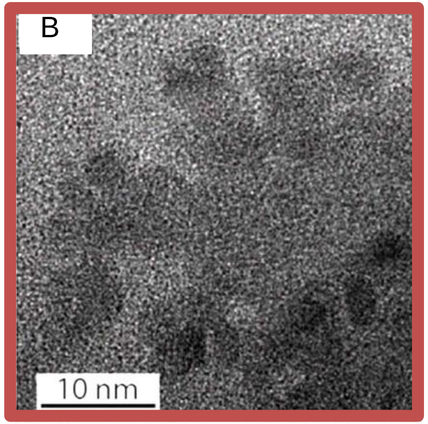
Correlation between *ex situ* and *in situ* results

Post mortem analysis of the nanostructures was performed to compare the morphology an chemical composition of nanoparticles.

Fig.A: HR-STEM image of the surface of a single PtNi nanoparticle synthesised *ex situ*. Fig.B: HR-TEM image of the PtNi surface synthesised in LC-TEM. Branched-like structure is visible in both cases.



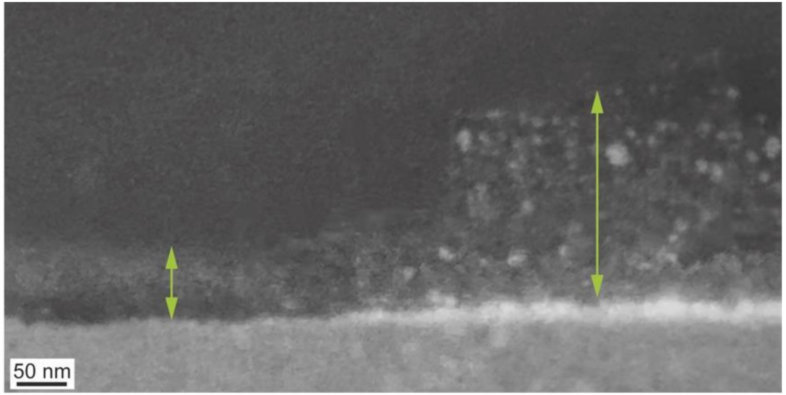
obraz HR-STEM warstwy otrzymanej w eksp. *ex situ*



obraz HRTEM warstwy otrzymanej w eksp. *in situ*

	Ex situ	In situ
Pt	85%	84%
Ni	15%	16%

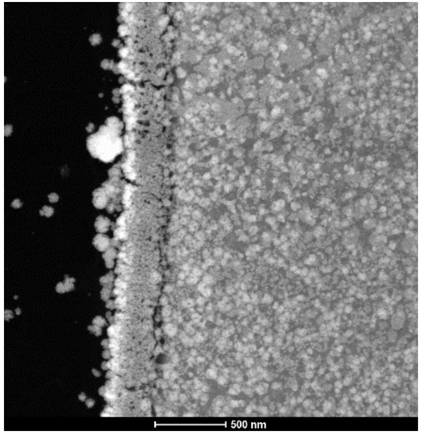
Electron beam influence



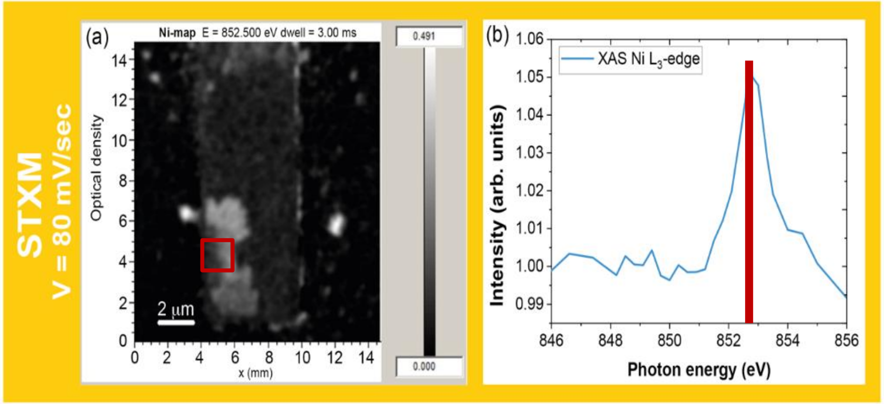
HAADF STEM image of the electrode edge with the electrodeposited PtNi nanograined film. Comparison between the structure stimulated (right arrow) and non-stimulated (left arrow) by the electron beam.

BF imaging of the PtNi nanoparticle during EDS scanning. The particle dissolves, under the focused electron beam.

In situ STXM at SOLARIS synchrotron centre



Post mortem SEM image of the working electrode's edge

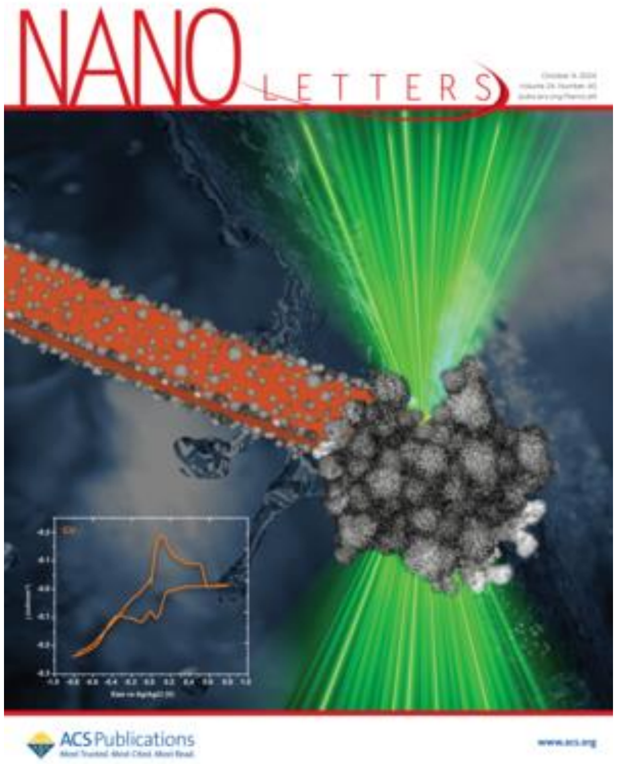


(a) STXM optical density map on the working electrode after cycling, for the photon energy in the Ni absorption peak (852.5 eV). It can be seen, that certain areas of the electrode is brighter, indicating the presence of NiO; (b) XAS spectrum taken from the edge of the WE (red box).

In situ electrodeposition was performed using STXM (Solaris DEMETER beamline) in order to analyse, what was the oxidation state of nickel in the nanoparticles. The working electrode edge was scanned after every voltammetric cycle to investigate time evolution of the 852.5 eV peak, which reportedly indicates the NiO $2p^63d^8 \rightarrow 2p^53d^9$ transition. This peak was visible throughout the synthesis process, which indicates, that the nickel oxide has been formed by electrodeposition and not by *post mortem* oxidation.

CONCLUSIONS

- ✓ The electrodeposition of PtNi alloyed nanoparticles film has been sucessfully transfered into the LC-TEM, which was confirmed by morphological (High Resolution TEM imaging) analysis.
- ✓ The PtNi film starts to grow directly on the Working Electrode edge. Due to the electron beam stimulation, clusters appear also above the electrode and slowly attach to the film surface.
- ✓ Focusing the beam on the specific nanoparticle during EDS acquisition may be damaging for it, causing its degradation or dissolution.



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