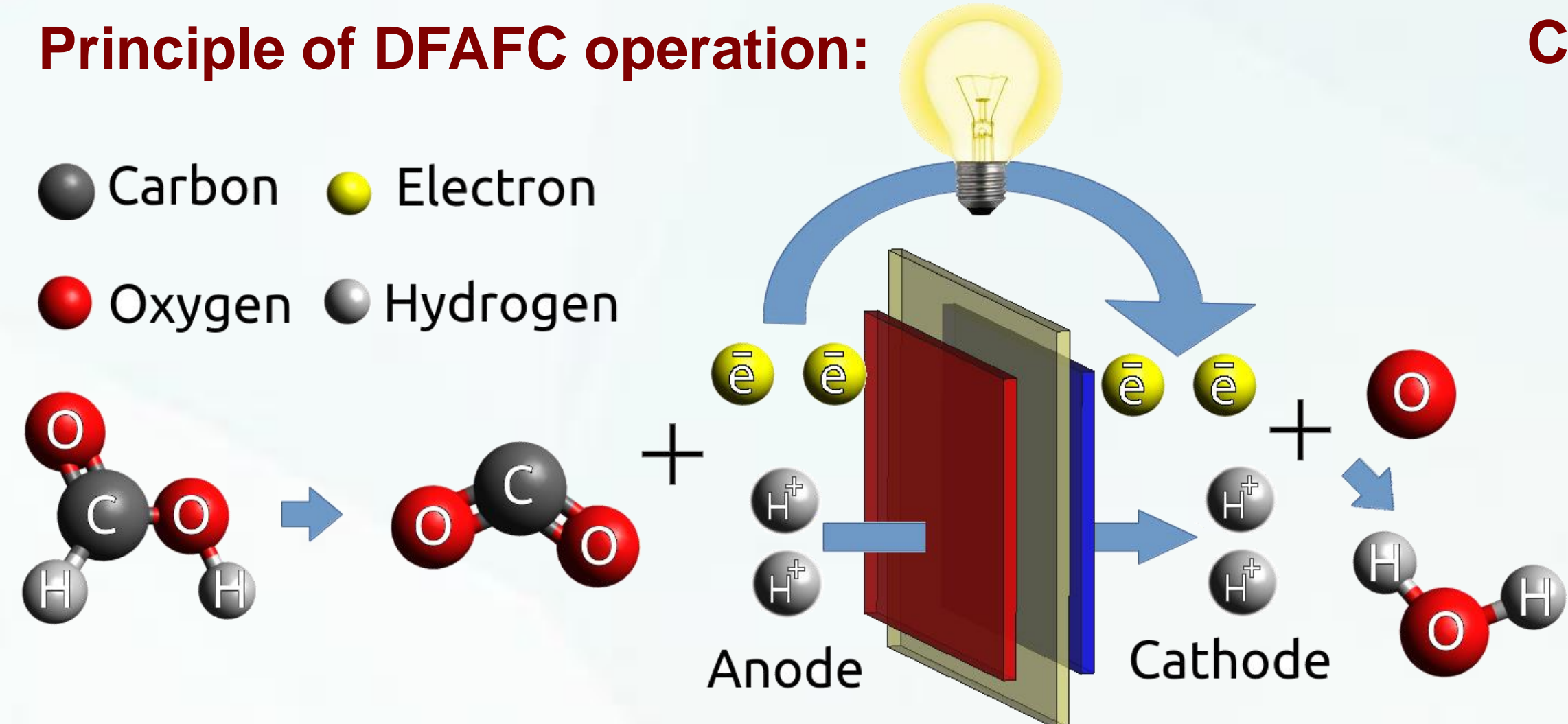


Transformations of the electrocatalysts during the work in fuel cells are very common. The structural information on the evolution of the catalyst state as a rule is obtained by ex-situ analysis when the catalyst is removed from the working environment. These works supply many valuable data however, the basic mechanisms leading to changes of catalyst activity are still not fully understood.

Principle of DFAFC operation:

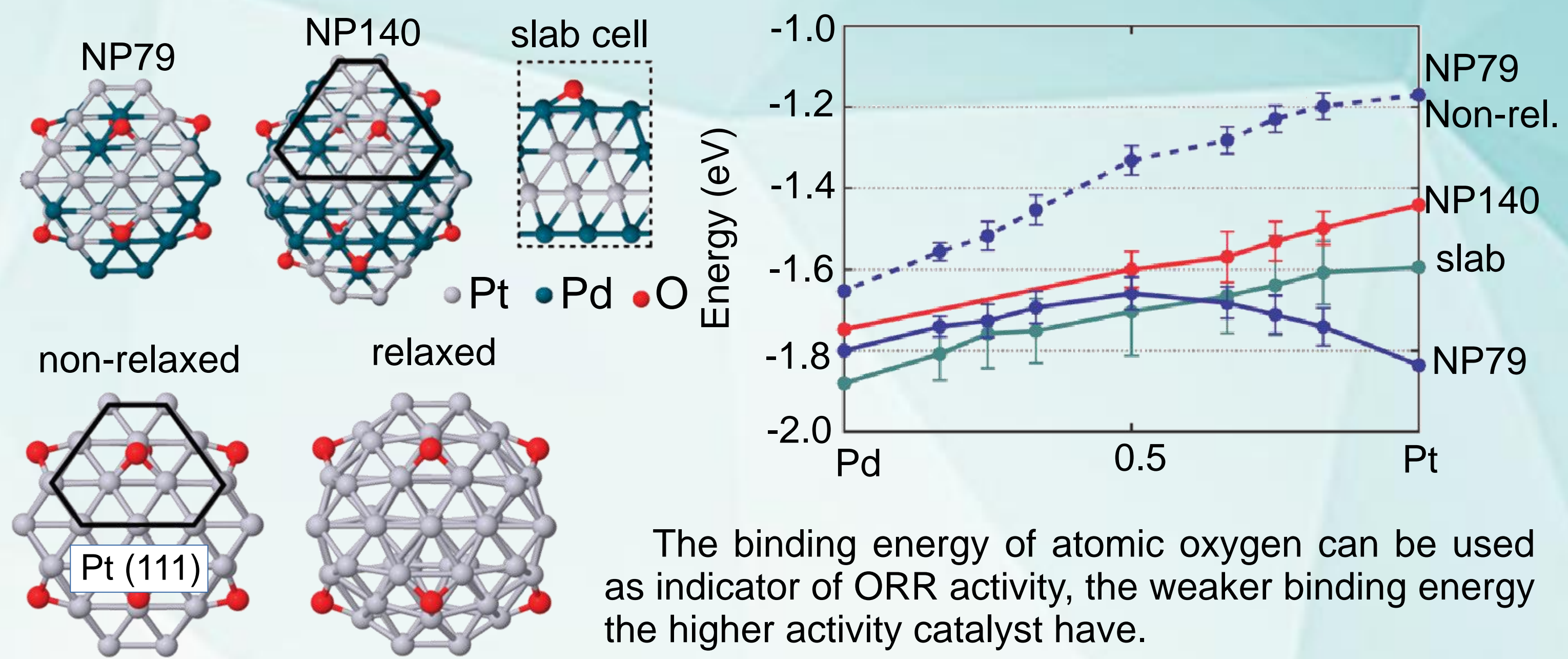
- Carbon ● Electron
- Oxygen ● Hydrogen



Changes of catalyst state:

- CO / O adsorption
- Metal dissolution
- Ostwald ripening
- Selective leaching of a metal in bimetallic systems
- Surface segregation

Role of geometric relaxation in oxygen binding to metal nanoparticles



The binding energy of atomic oxygen can be used as indicator of ORR activity, the weaker binding energy the higher activity catalyst have.

In case of small NP79 crystal the curve of relaxed model has a convex shape and has stronger binding energy that in the non-relaxed case. Therefore, the relaxed model is significantly less active than the non-relaxed one.

J. Phys. Chem. Lett., 2011, 2 (11), pp 1237–1240

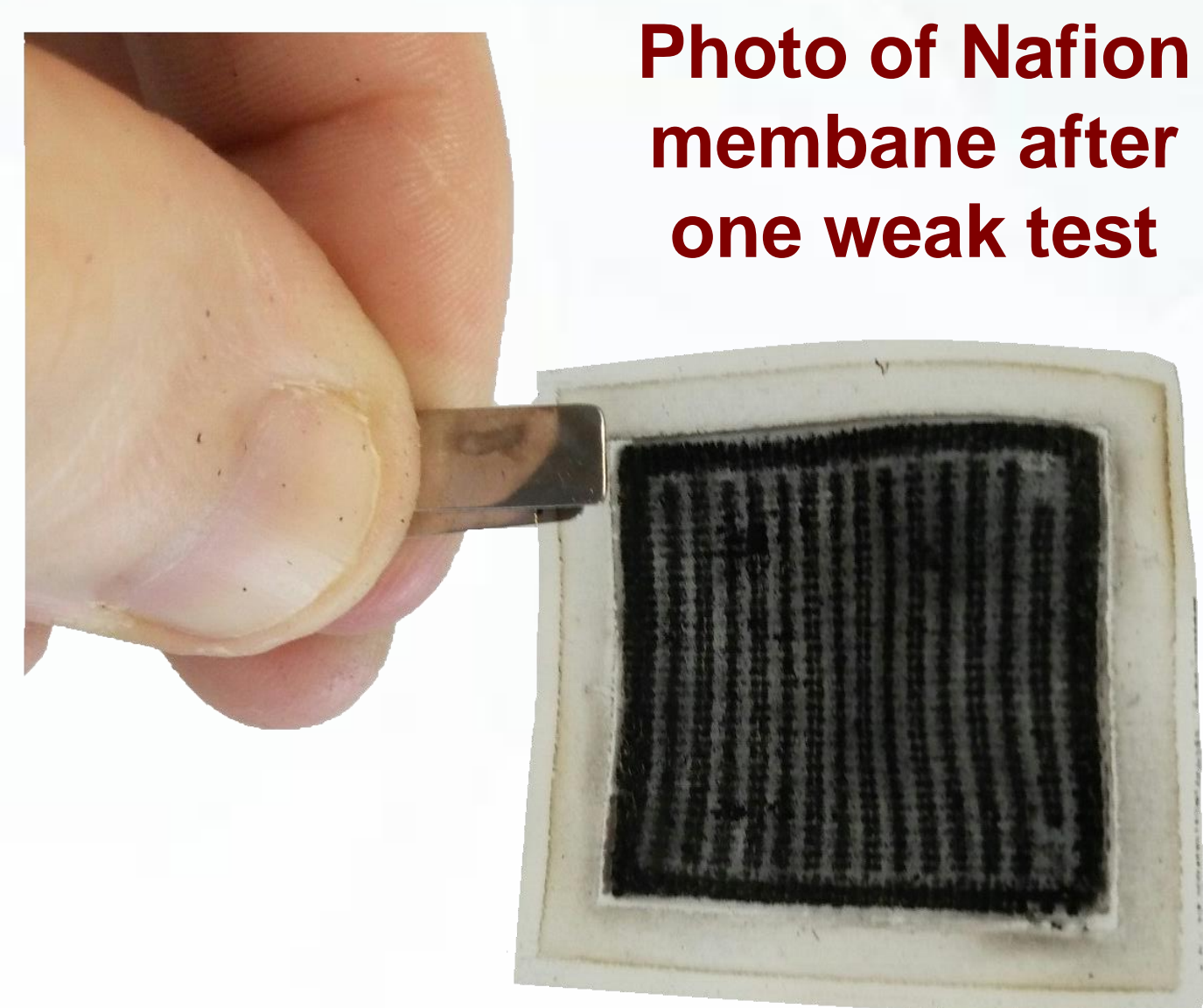
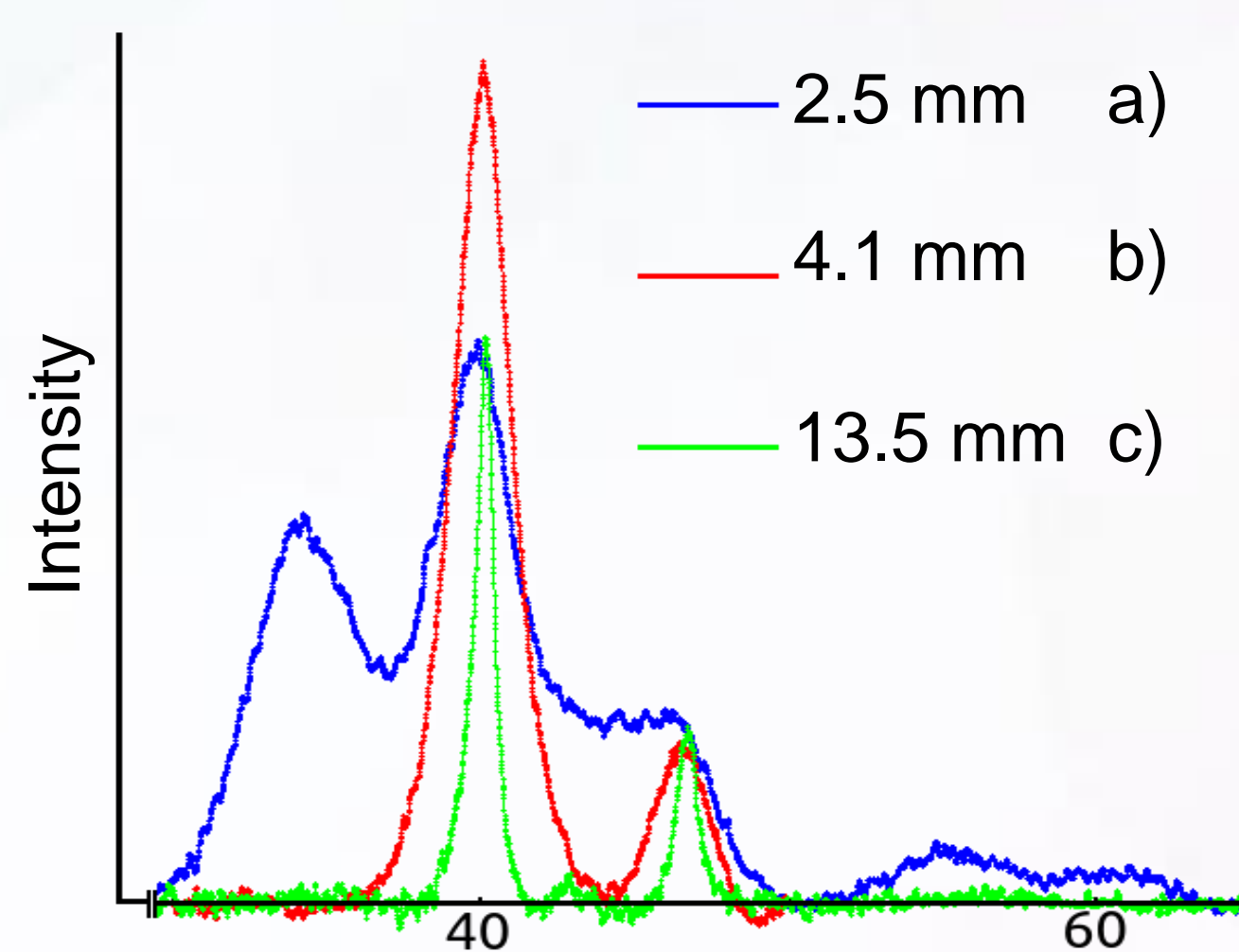


Photo of Nafion membrane after one weak test

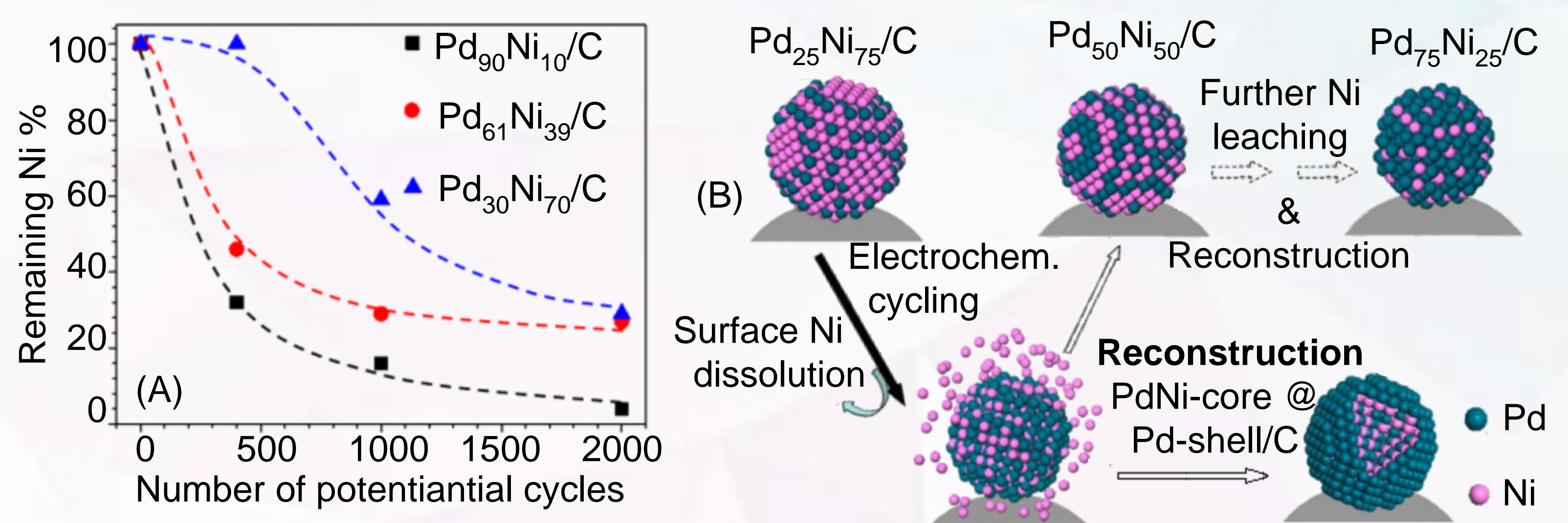
After few CV and/or normal DFAFC measurements some amount of anode catalyst detaches from carbon cloth and strongly adsorbs on Nafion membrane.

Growth of Pd/C nanoparticles



XRD patterns of a) initial Pd/C catalyst, b) after Formic acid exposure (~3 min) and c) after one weak use in DFAFC

Composition-structure-activity relationships of Pd-Ni in ORR

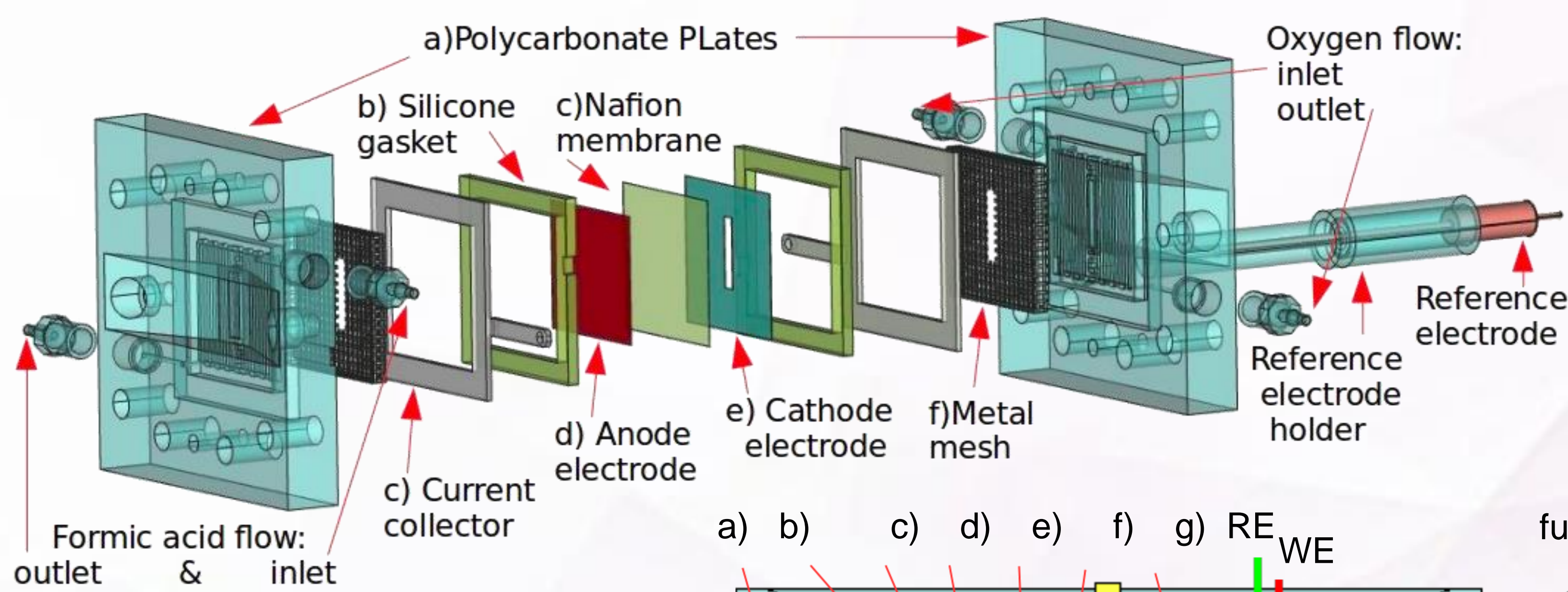


It was found that during CV tests the effect of Ni leaching depends on the initial composition and differently changes activity - (A). Using *in-situ* PDF analysis the model of Ni leaching was derived - (B): when some amount of Ni is removed the catalyst crystal may reconstruct either to the Pd-rich shell structure (right bottom picture) or to the Ni-poor alloy (right top picture) through a set of stable or semistable states.

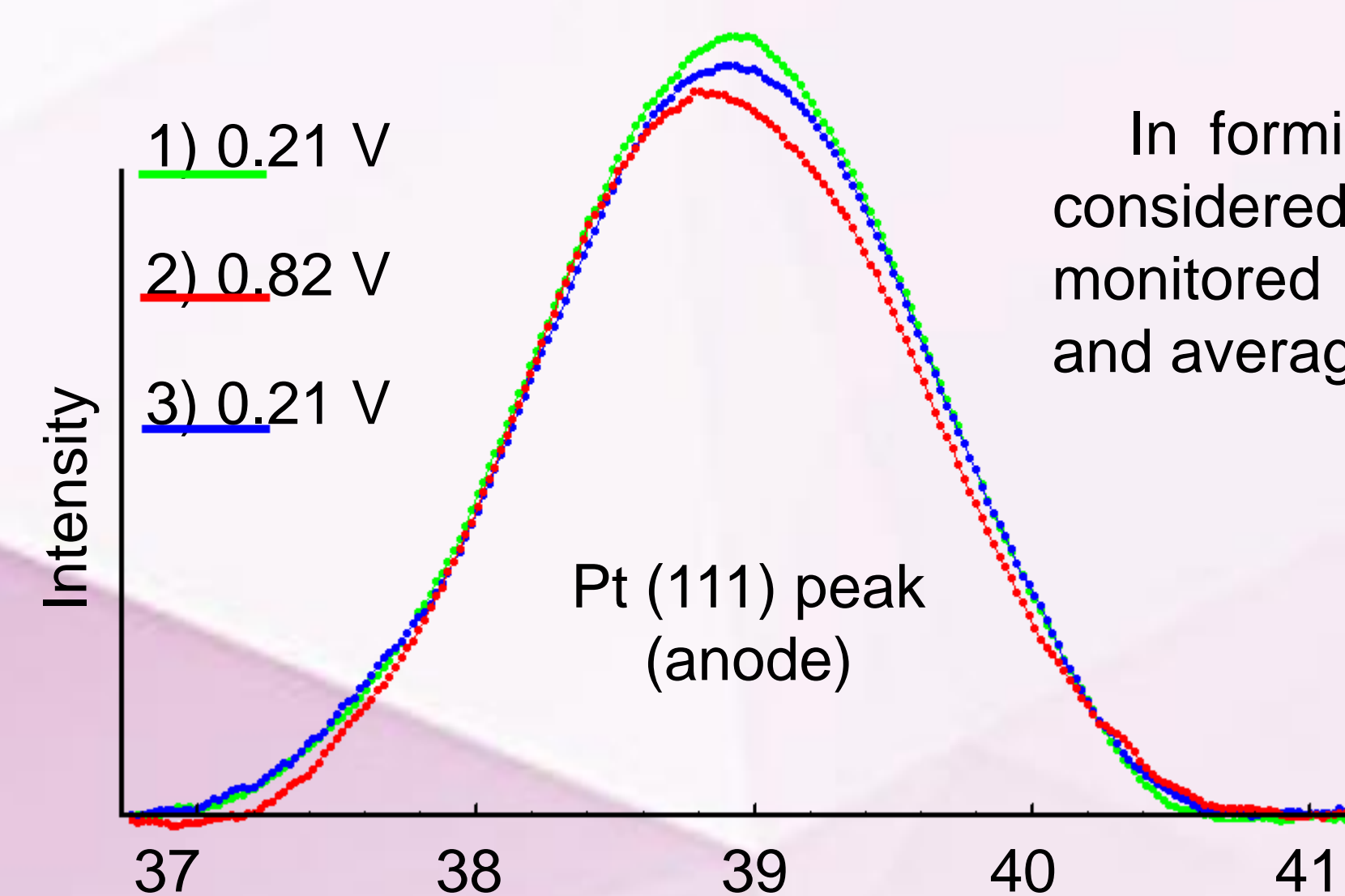
ACS Catal., 2015, 5 (9), pp 5317–5327

Subtle and environment dependent (!) phenomena can be measured and evaluated only under *operando* conditions. For these purposes the special *in-situ* XRD camera was designed. Overall design of the camera almost fully mimic the ordinary DFAFC for traditional electrochemical studies.

The scheme of *in-situ* XRD camera



Cross-section of the cell. X-ray beam passes the XRD cell through a window at the center of (a) of 0.33 mm thickness. We avoid beam scattering on the steel meshes (g) and cathode (d) by providing rectangular openings in both.



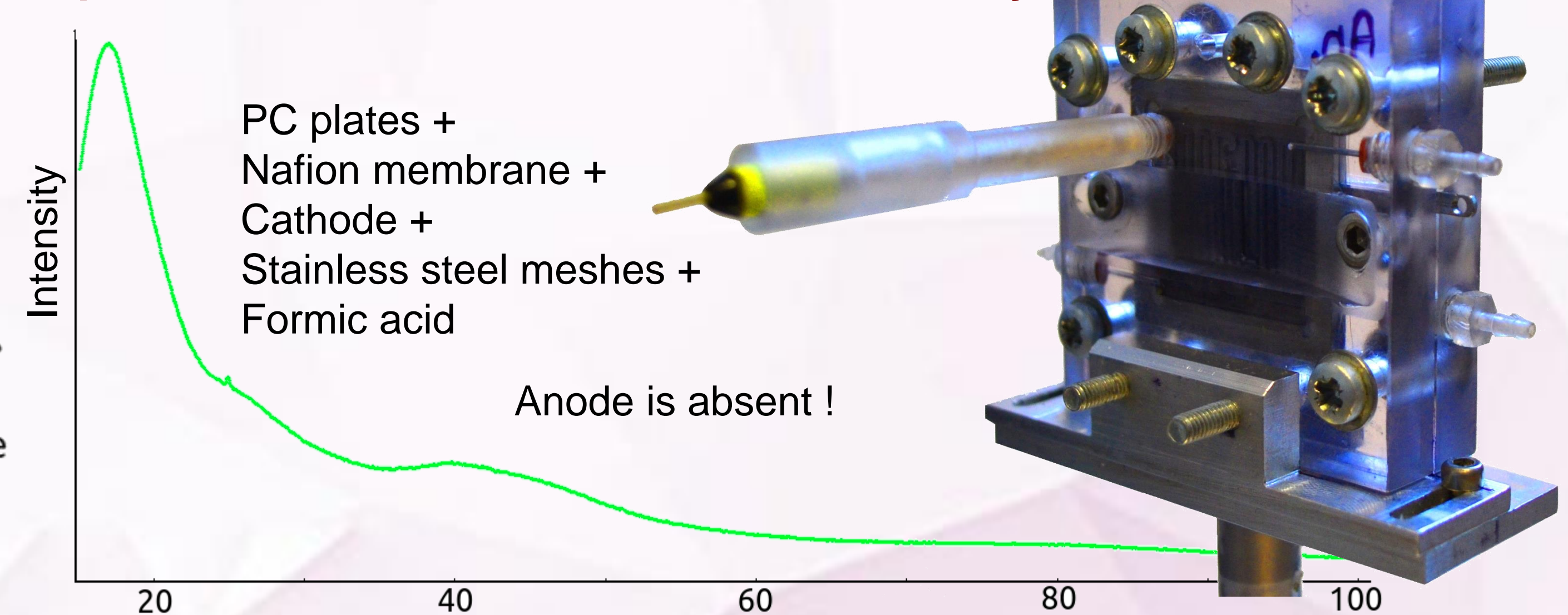
In formic acid oxidation reaction the 111 face is considered as most active one. The (111) peak was monitored from 37.5 to 42 degree, repeated 6 times and averaged later (XRD pattern of Pt (111) peak)

	Centre of the peak	Area of the peak	FWHM of the peak
1) 0.21 V	39.96	1734	1.67
2) 0.82 V	39.90	1602	1.64
3) 0.21 V	39.96	1670	1.67

After the first measurement (0.21 V) at 0.82 V potential the peak position have shifted by -0.06 degree, area and width also changed. There are at least two possible reasons for these changes. The first one: at the potential higher than 0.45 (roughly) a surface metal oxide was formed and it leads to the peak position shift. The second one: the charging/recharging of the nanocrystals changes d-band density and affects interatomic distance and the peak shift. Probably, both mechanisms coexist.

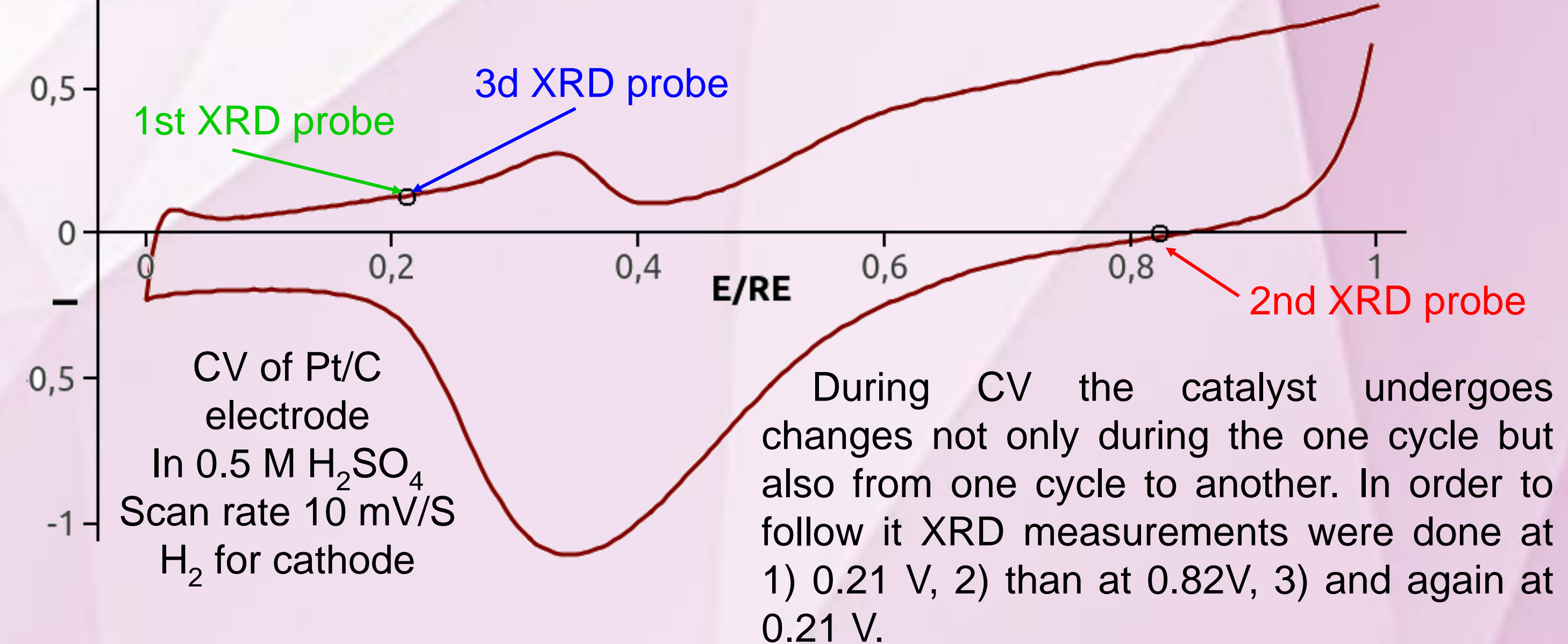
After the second measurement (0.82 V) at the start potential (0.21 V) the peak parameters (position and width) returned back to the initial state. Only area of peak was lower than initial one (0.21 V) that indicates the losing of the catalyst.

XRD pattern of "blank" DFAFC in-situ assembly:



Since background line does not contain any intensive and/ or narrow peaks the further *in-situ* analysis of anode electrode can be performed without additional restriction.

CV within the in-situ XRD camera



● The designed XRD camera-DFAFC allows to collect in situ data not available otherwise. The single studies of either activity or ex-situ structure / composition changes are not able to shed the light on complex transformations of the catalyst in fuel cell. Subtle phenomena (such as reconstruction, relaxation and so on) that take place in catalysis exist only under *operando* condition and if catalyst is removed from the system these phenomena disappear.

● All these obtained data require precision, attention, repetitions and comparisons with CV/TEM data since even the first set of 3 in-situ points analysis shows a complex nature of metal oxidation in fuel cell.

● Only *in-situ* measurements can explain the details to the composition-structure-activity relationship. The current *in-situ* XRD camera can be successfully used for electrochemical and XRD measurements simultaneously so it doubtlessly will help us to improve our understanding of catalyst changes in FC.