Novel Highly D-Loaded/High D-Diffusivity Nanostructured Materials on the Pd substrate as a Potential Media to Enhance Low Energy Nuclear Reactions

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Introduction

- After more than 18 years studies of CMNS effects many issues concerning their nuclear nature are still at the table.
- Among others: to show *in-situ* statistically significant nuclear signatures in one electrolysis run. It is hard to provide charged particle detection in-situ due to presence of the electrolyte, failure of the detector contact with the Pd foil cathode and possible mechanical damage of track detector's surface (in case of too tight detector attachment)
- Are the charged particles emitted after electrolysis have the same origin as that emitted in-situ ?

How to enhance CMNS effects

- Pristine Pd cathodes (even with a special treatment, such as annealing and etching) do not show measurable nuclear emissions during and after D-loading
- Good reproducibility of charged particle emissions was achieved during controlled exothermic D-desorption from Pd/PdO:D_x heterostructure after electrochemical loading (A. Lipson et al, ICCF-12 Proc), thus giving evidence for a high D-diffusivity advantage.
- To enhance CNMS effects in electrochemical processes, we now propose to switch to the novel Pd based nanostructured materials (as the cathodes), allowing a large deuterium loading and/or high D – diffusivity at the surface resulting in a large DD-screening, drastic changes in phonon spectra as well as high quantum entanglement of deuteron pairs.

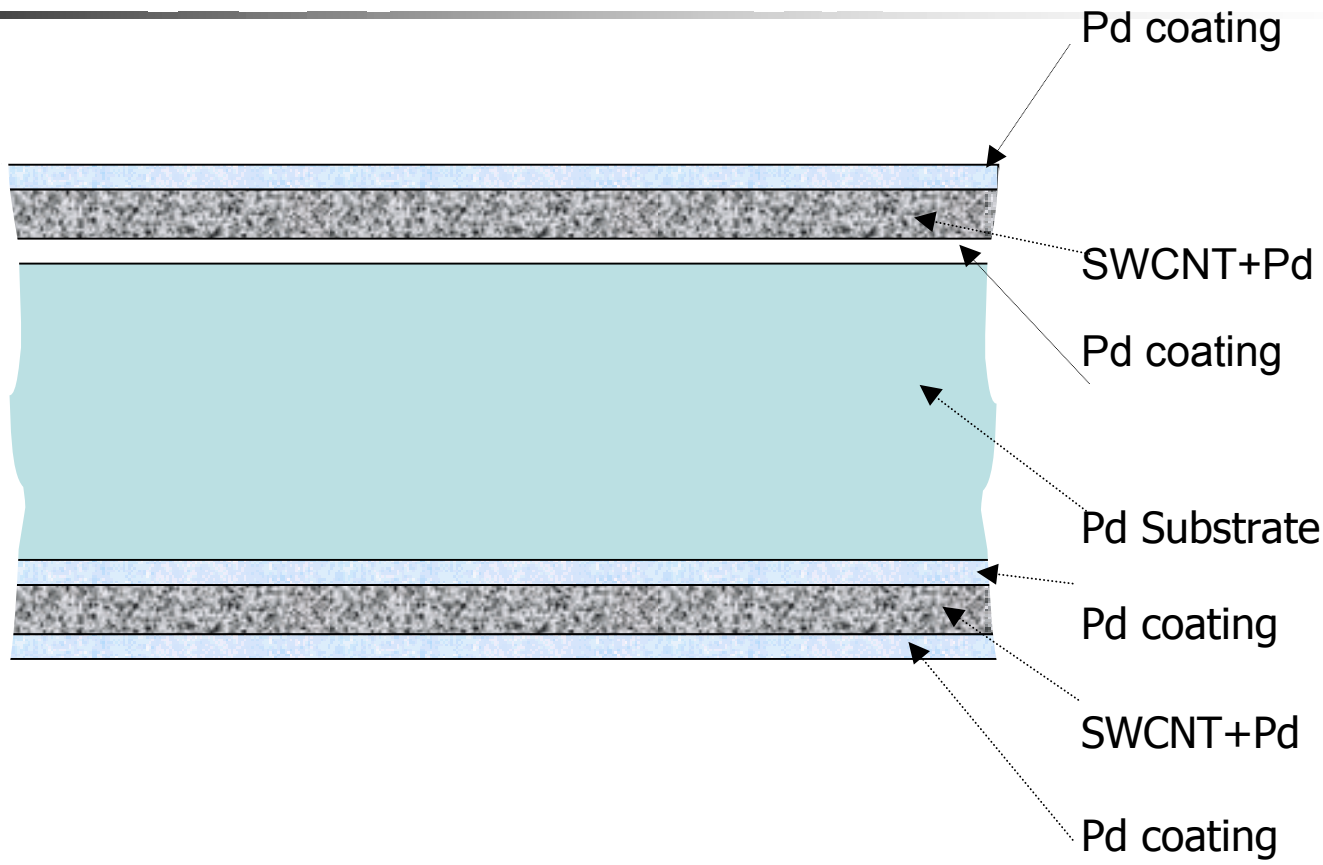
Objectives

- To synthesize novel highly D- loaded/ high D-diffusivity nanostructured cathodes deposited on top of Pd substrate in order to enhance CMNS effects.
- To study hydrogen loading (if any) into SWCNT encapsulated by Pd coatings.
- To develop a special holder for CR-39 detector attached to the cathode by a right way allowing in-situ charged particle detection excepting electrolyte penetration and mechanical damage.
- To obtain reproducible nuclear emissions in controlled conditions of in-situ electrolysis (in one run) and after the loading.

Samples

- A pristine Pd cathode (Alfa-aeser, 99.95 %) annealed at t = 900 C and etched in aqua regia.
- A high capacity hydrogen storage media consisting of Single Wall carbon nanotube (SWCNT) layer encapsulated by thin Pd films electrodeposited on top of Pd foil (Pd-SWCNT composite).
- A multilayer Pd-Re-Pd-Re structure electrodeposited on top of 50 micron Pd foil (5 Pd-Re multilayer of 100 nm thick). This structure provides high H/D diffusivity during deuterium permeation through it (2 times higher than pristine Pd at the same T)

Pd′/SWCNT/Pd′/Pd/Pd′/SWCNT/Pd′ composite material



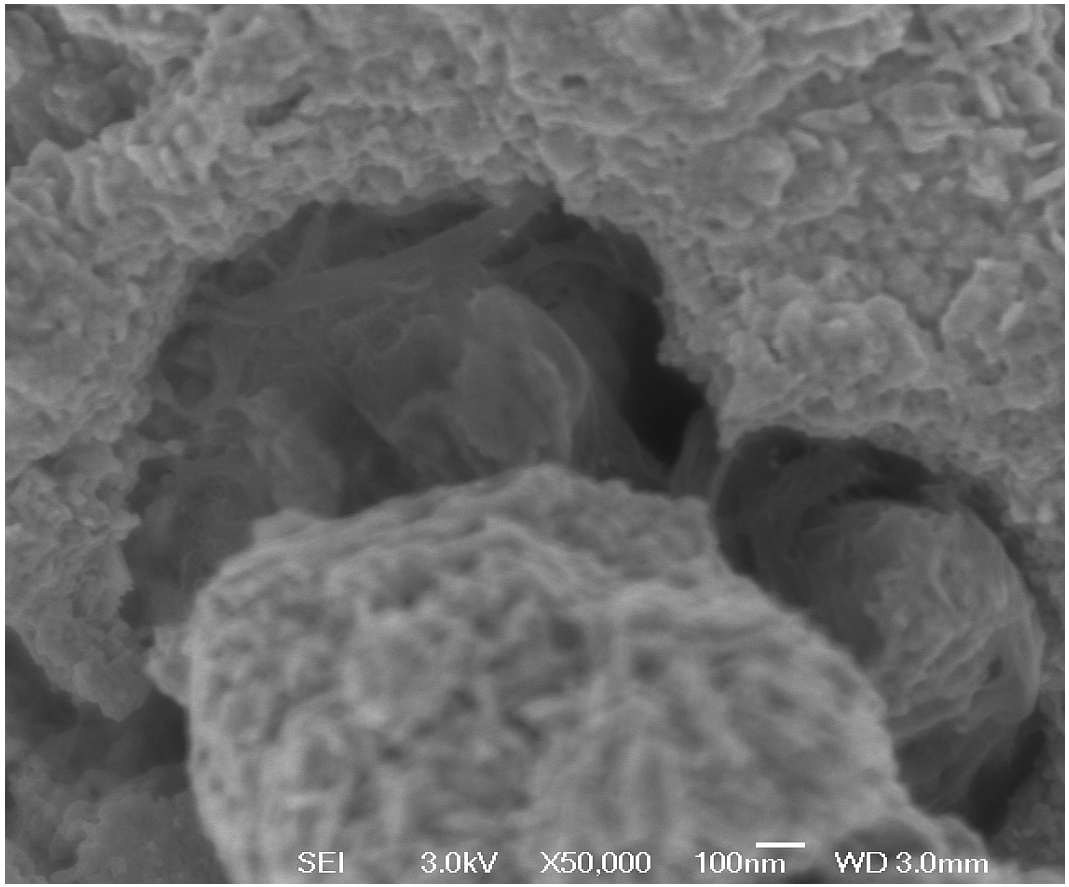
Pd′/SWCNT/Pd′/Pd/Pd′/SWCNT/Pd′ composite foil; SWCNT (Ø = 1.3 nm) types:

- (1) HiPco™ Bucky™ tubes, lot #79, Carbon Technologies Inc., (length range 0.5-1.5 μm, purity 95%).
- (2) 7782-42-5, Helix Material Solutions, Inc., (length range 2-20μm, purity 90%) .
- (3) Alfa-Aeser (length range 15-40 μm, purity 95%)
- Opened by etching in concentrated nitric acid

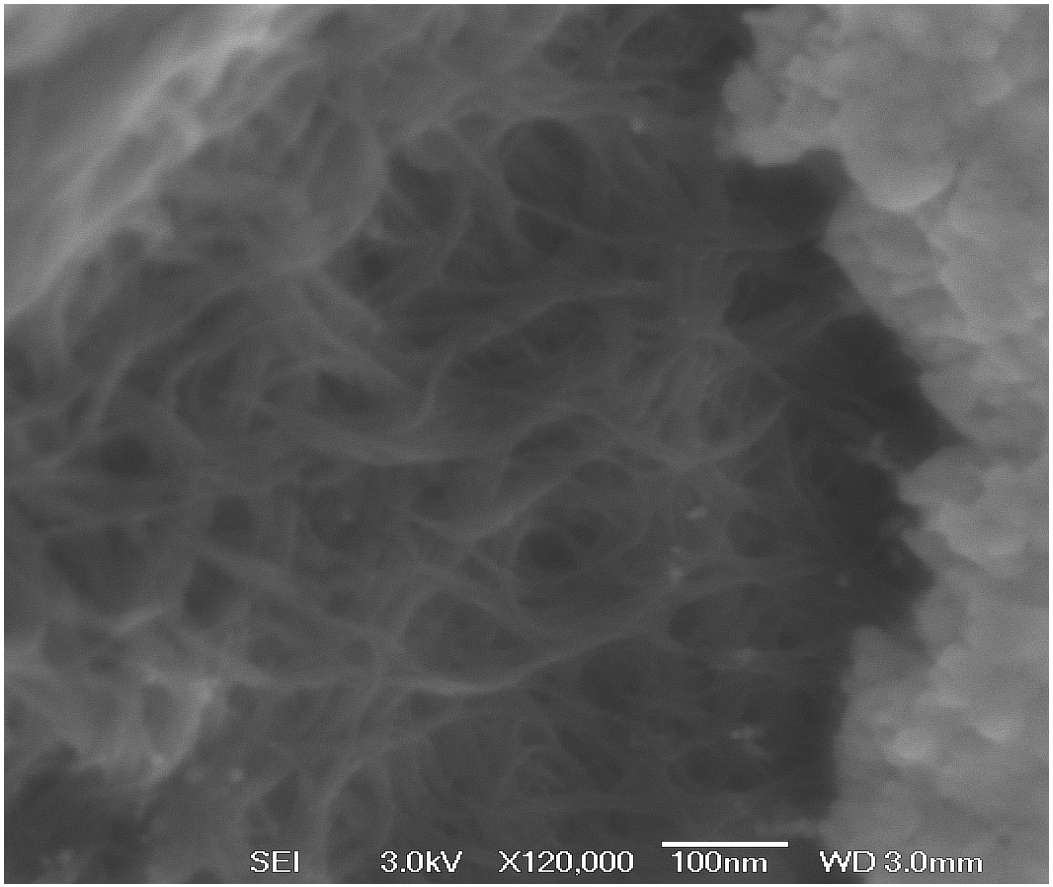
Volumetric hydrogen concentration in the Pd′/SWCNT/Pd′/Pd/Pd′/SWCNT/Pd composite and the Pd′/Pd/Pd′ reference samples loaded by electrolysis at a constant temperature, T=290K.The Electrolysis charge transferred through the cathode is Q = 45 C/cm2.

Sample type	Mass[g]	Desorbed H_2 Volume, [cm^3]	<x>=[H]/[Pd]	C_H, [% wt.]
Pd′/Pd/Pd′	0.208	14.61±0.21	0.68±0.01	-
Pd′/SWCNT/Pd′/Pd/Pd′/SWCNT/Pd′-(1), M(SWCNT)=2.8 mg	0.207	18.40±0.32	0.86±0.03	12.0±1.4
Pd′/Pd/Pd′	0.142	9.83±0.12	0.66±0.01	-
Pd′/SWCNT/Pd′/Pd/Pd′/SWCNT/Pd′-(2), M(SWCNT)=2.2 mg	0.146	11.80±0.20	0.79±0.02	8.0±1.0
Pd′/Pd/Pd′	0.140	9.80±0.13	0.66±0.01	-
Pd′/SWCNT/Pd′/Pd/Pd′/SWCNT/Pd′-(3), M(SWCNT)=1.8 mg,	0.141	11.39±0.23	0.78±0.02	7.8±1.2
Pd′/Pd/Pd′	0.145	10.13±0.24	0.66±0.02	-
Pd′/SWCNT/Pd′/Pd/Pd′/SWCNT/Pd′-(1*), M(SWCNT)=1.8 mg (non-etched)	0.148	10.04±0.20	0.65±0.02	0

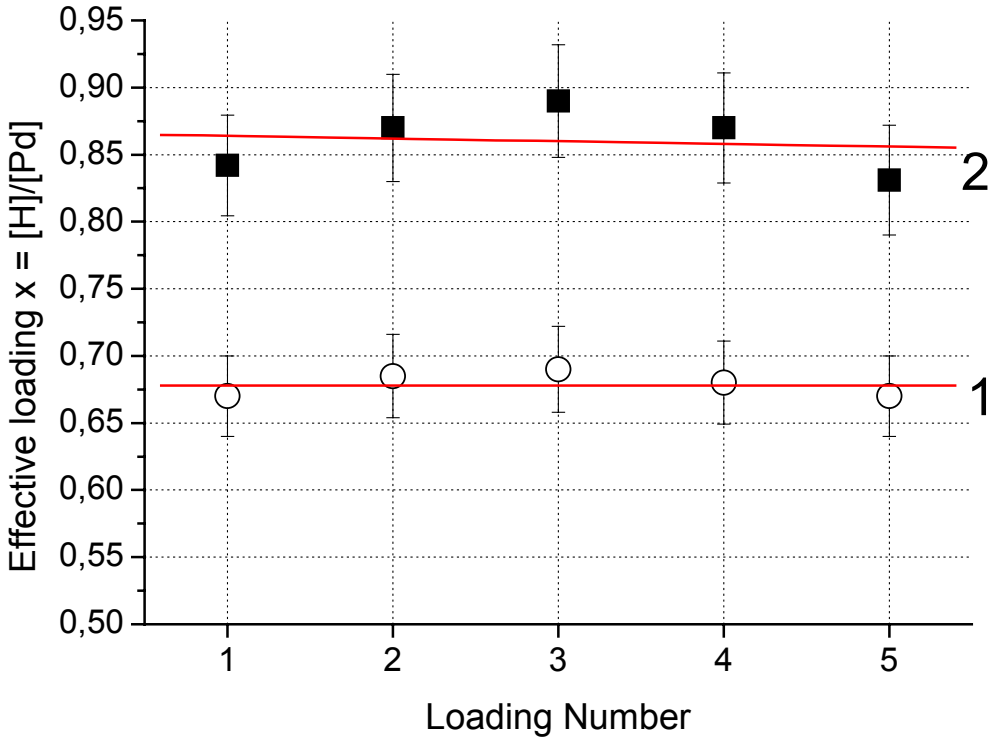
SEM images of the Pd-SWCNT interface after 1 min - etching in nitric acid: (a) magnification at x 50000



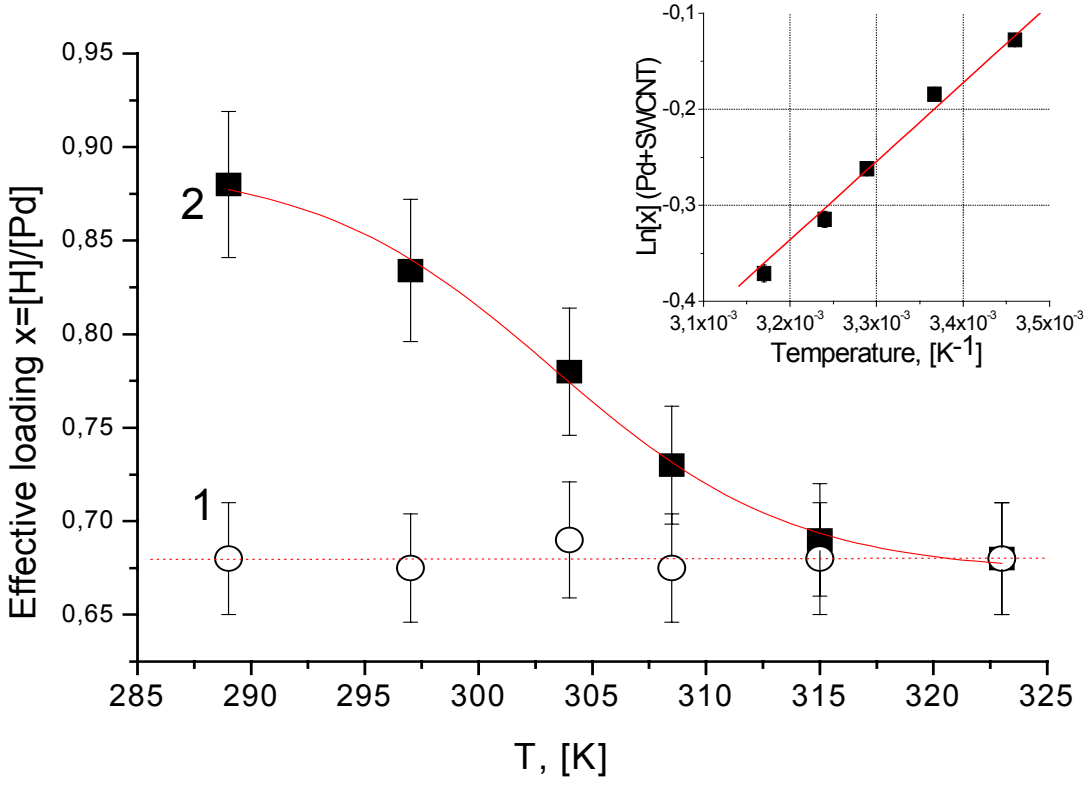
SEM image of the Pd-SWCNT interface after 1 min - etching in nitric acid: (b) magnification at x 120000.



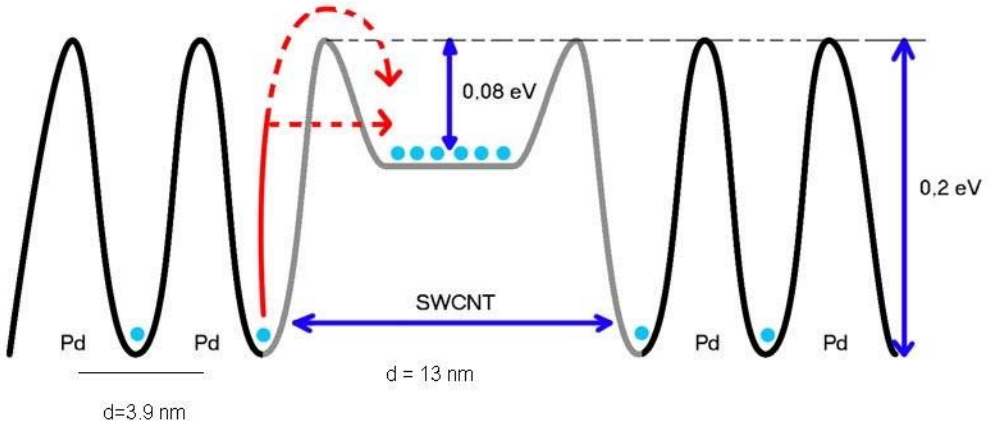
Hydrogen loading reproducibility for the Pd′/SWCNT/Pd′/Pd/Pd′/SWCNT/Pd′ with SWCNT- (1), (curve 2) and for the reference sample of Pd′/Pd/Pd′ (curve 1): 5 consecutive loading-deloading cycles. The loading: electrolysis at j=5.0 mA/cm2 for 2.5 h. The deloading: vacuum heating at T=673 K.



Effective hydrogen loading in the Pd′/Pd/Pd′ (curve 1) and in the Pd′/SWCNT/Pd′/Pd/Pd′/SWCNT/Pd′ with SWCNT (1) (curve 2) samples vs the loading temperature. Inset shows Arrhenius plot for the curve 2 data in the coordinates (1/T, Ln[x]). The linear fit is consistent with the activation energy of hydrogen absorption ε_H = 0.14 ± 0.02 eV/H_2-molecule.



Energy diagram of a hydrogen transport in the Pd-SWCNT-Pd nanostructure



H/D storage in Pd-SWCNT cathode and its consequences with respect to CMNS

- Electrochemically loaded SWCNTs encapsulated by thin Pd coatings onto a Pd foil provides a reproducible high gravimetric capacity (8-12 % wt.) with respect to hydrogen: $(H/C)_{max}$ = 1.5.
- Hydrogen absorption occurs mainly within the inner space of the SWCNT and depends on the SWCNT length.
- The activation energy of the hydrogen desorption from the SWCNT is 0.14 eV/H_2-molecule, thus indicating a weak hydrogen binding in the nanotubes.
- These peculiarities of D-loading and binding in SWCNT suggest a high energy concentration over D-loaded nanotubes resulting in both large electron screening of deuterons and phonon focusing inside the SWCNT encapsulated by Pd.

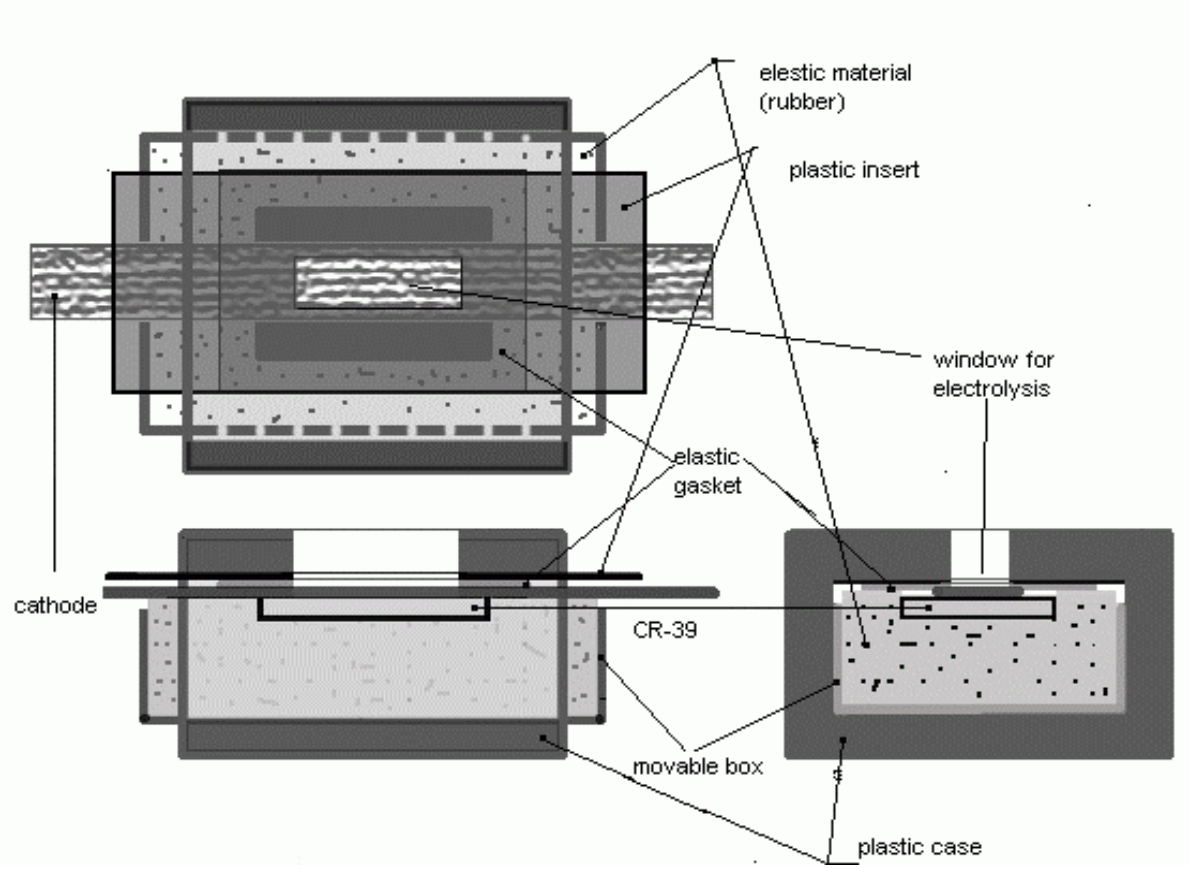
Nuclear Detection

- Charged particle detection: CR-39 (Landauer inc) with set of metal foil filters (Al 33 μm , Cu 25 μm thick) in order to estimate type and energy of emitted particles.
- Two types of experiment:

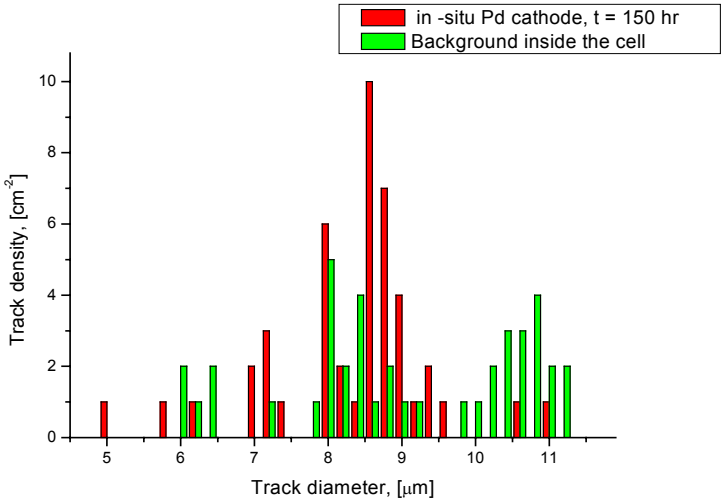
(a) in-situ electrolysis with Pd-SWCNT and Pd-Re cathodes during 122 hr in 0.3 M LiOD/D2O electrolyte at j = 30 mA/cm^2.

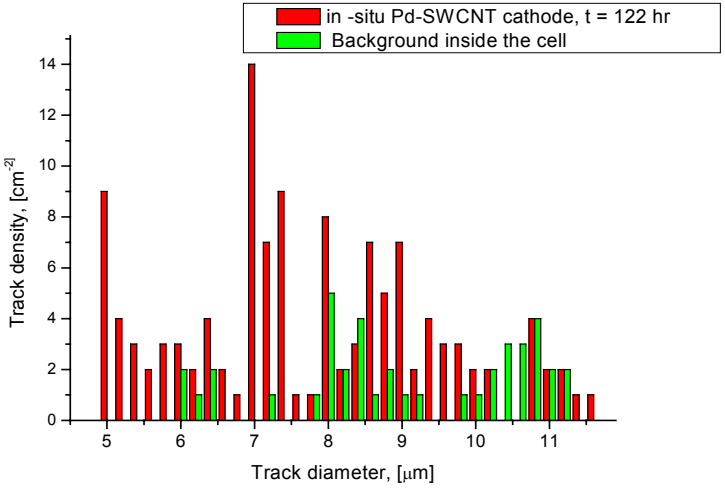
(b) Exothermic D-desorption from the cathodes after the short electrolysis (terminated as soon as loading reach x=D/Pd= 0.7).Time of exposure t = 10 x 3600 s, (t chosen accordingly maximal D-desorption rate).

Design of the CR-39/cathode holder assembly for in-situ electrolysis measurement

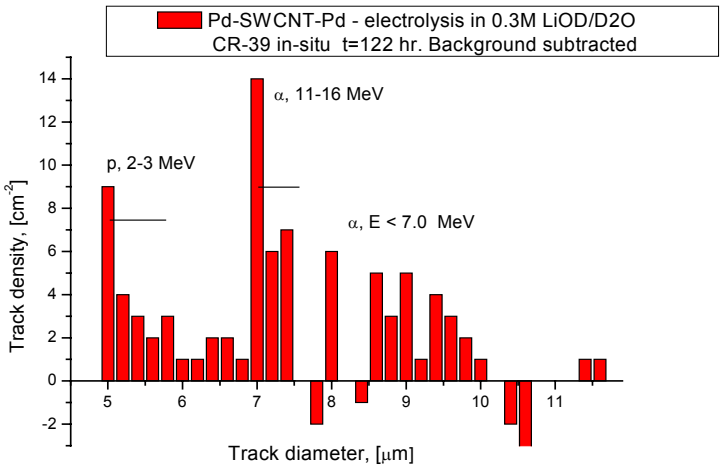


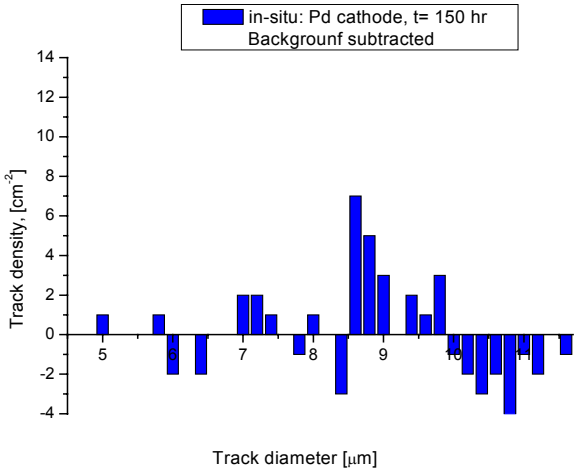
In-situ electrolysis with the pristine Pd (left) and Pd-SWCNT (right) cathodes



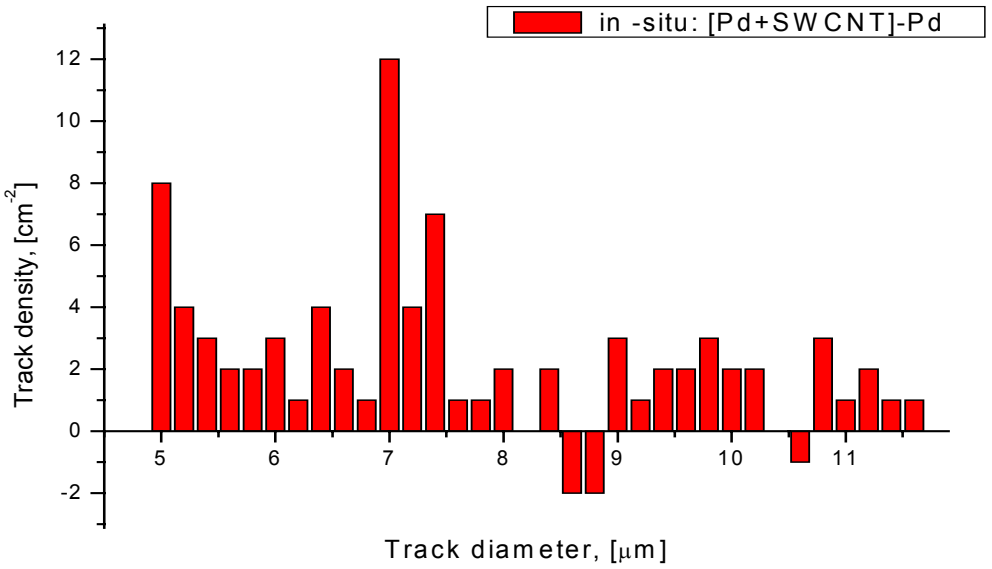


Pd: No statistically significant emissions (besides absorbed natural alpha nuclides) is detected.
Pd-SWCNT: Statistically significant emissions of protons and energetic alphas in the one 122 hr run: $\langle N_p \rangle = (5.24 \pm 1.09) \times 10^{-4}$ p/s-cm^2, $\langle N_\alpha \rangle = (1.04 \pm 0.15) \times 10^{-3}$ α/s-cm^2

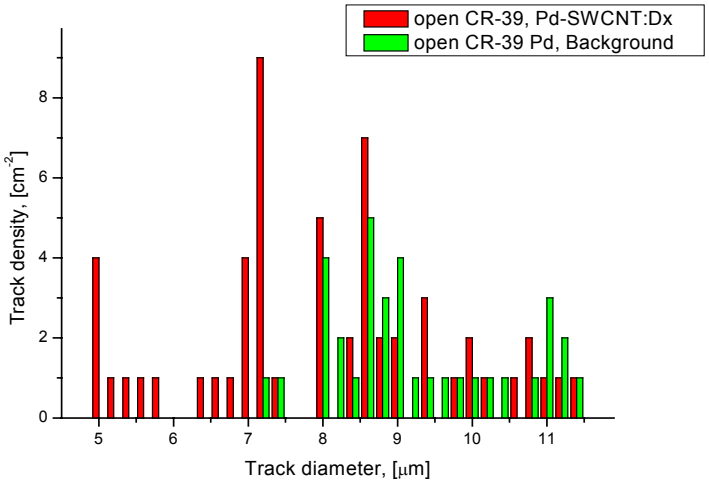


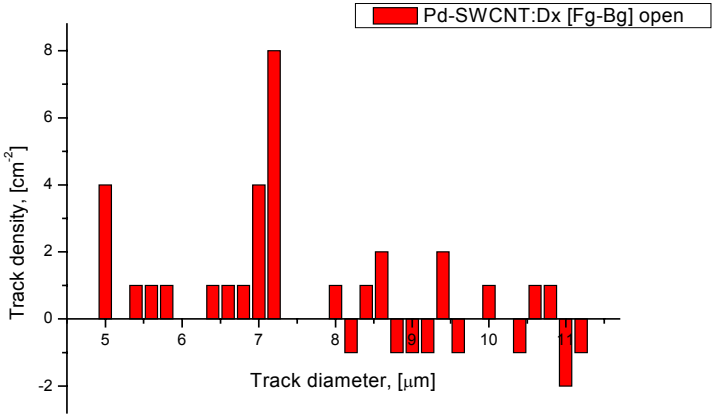


Net SWCNT (D/C = 1.5) contribution in charged particle emissions: the Pd cathode CR-39 result is subtracted from that of the Pd/SWCNT/Pd

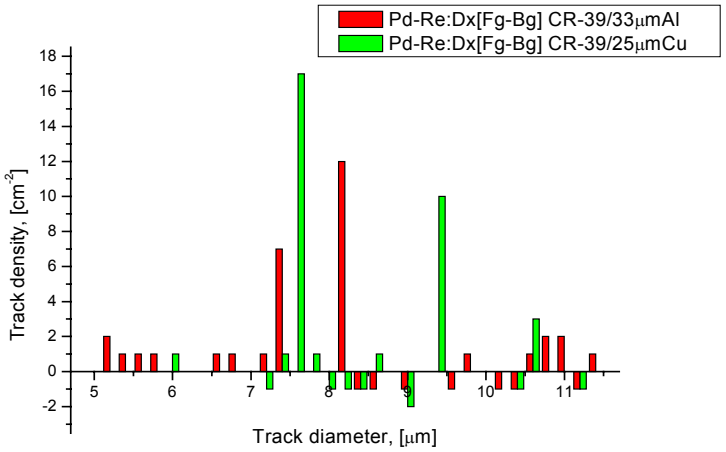


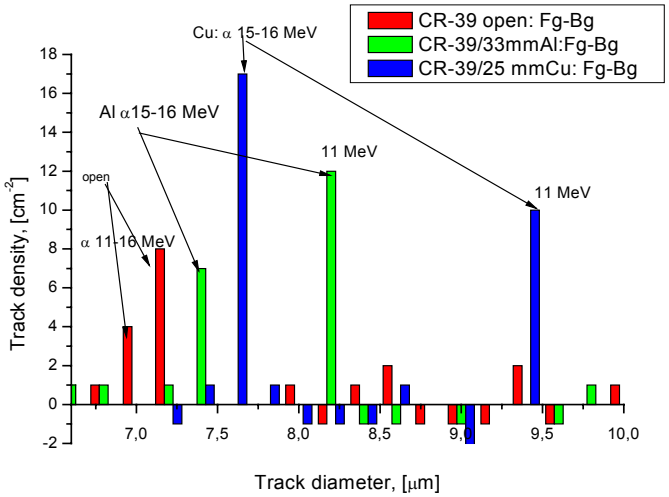
Pd/SWCNT/Pd after electrolysis: t = 10 x 3600 s, open CR-39 data: $<N_p>$ =(1.7±0.7)x10^{-3} p/s-cm^2; $<N_\alpha>$ = (2.8±0.9)x10^{-3} α/s-cm^2



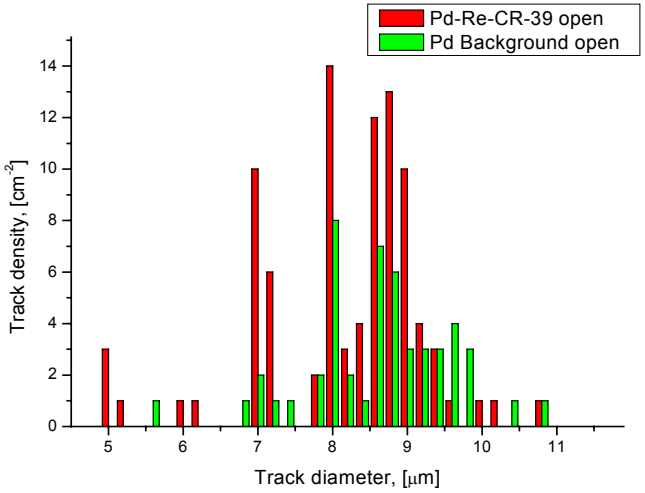


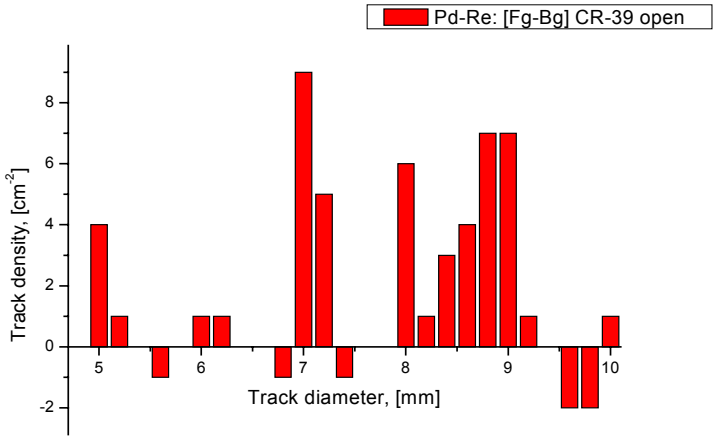
Pd/SWCNT/Pd:D_x after electrolysis: t = 10 x3600 s, 33μm Al and 25μm Cu filtered CR-39 data. Right graph shows 11-16 MeV alpha identification



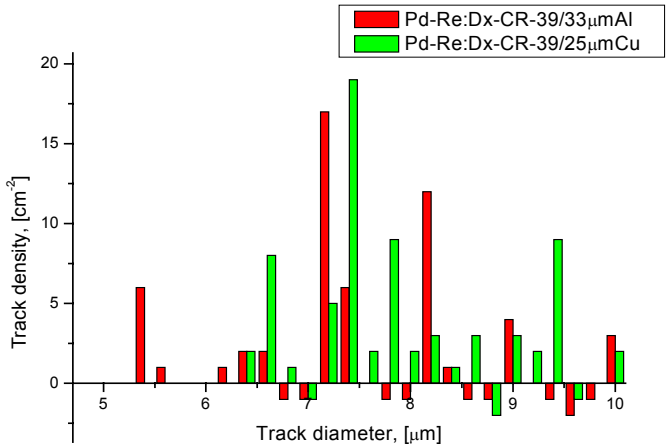


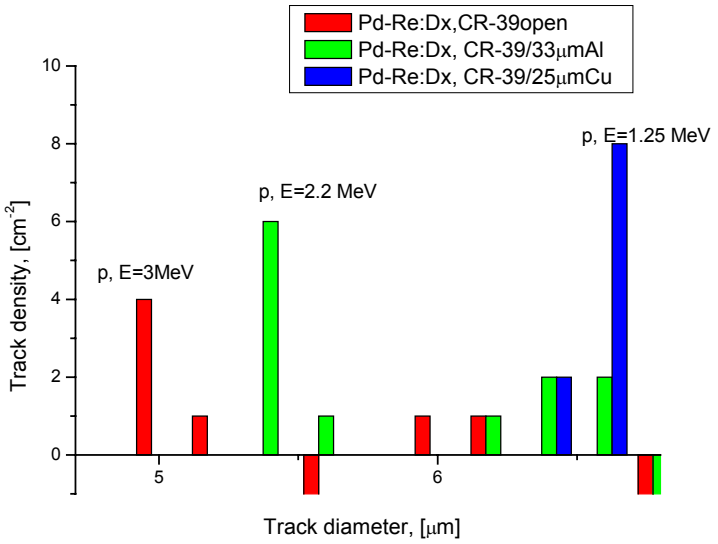
Pd/Re/Pd:D_x after electrolysis: t = 10x3600 s, open CR-39 data:
$\langle N_\alpha \rangle = (3.43 \pm 0.76) \times 10^{-3}$ α/s-cm^2



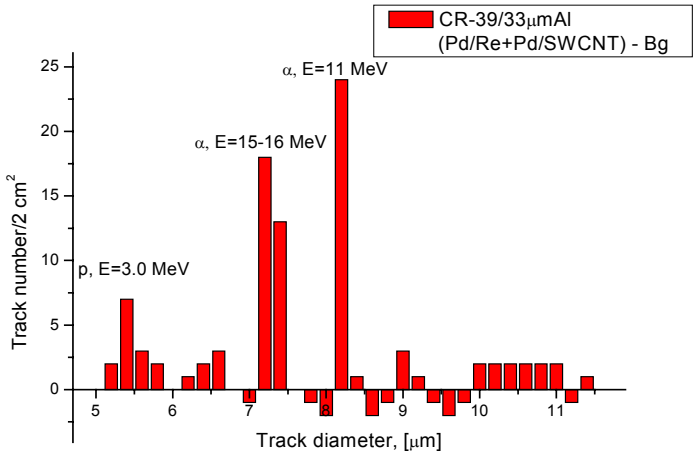


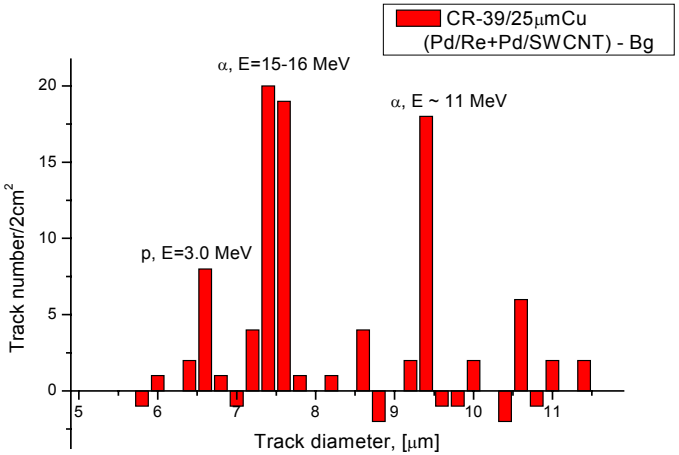
Pd/Re/Pd:Dx after electrolysis: t = 10 x3600 s, 33μm Al and 25μm Cu filtered CR-39 data. Right graph shows 3 MeV proton identification



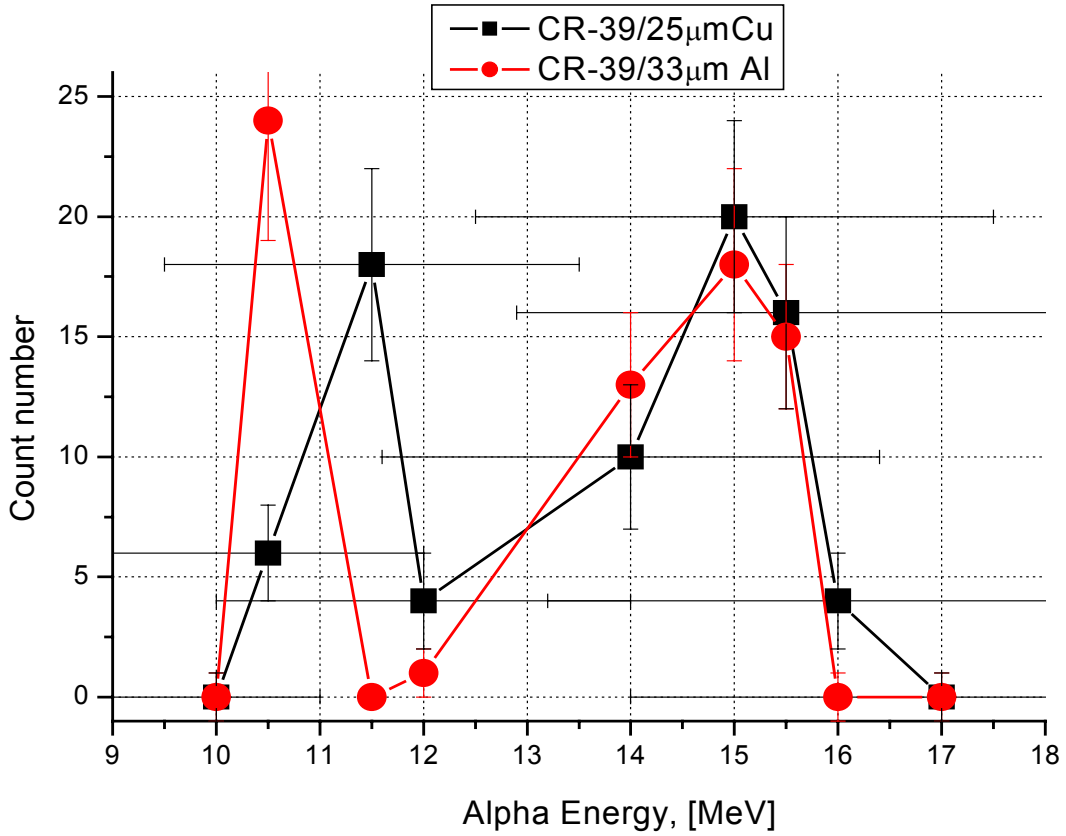


CR-39 track diameter distributions (with the Backgrounds subtracted) for the sum of the Pd/Re:D_x+Pd/SWCNT:D_x runs





Reconstruction of alpha spectra for the CR-39 detectors with 25μm Cu and 33 μm Al filters



Results on in-situ nuclear measurement

- First in-situ CR-39 measurements showed that the Pd/SWCNT/Pd cathode during electrolysis generates both 3.0 MeV (DD) protons and high energy alphas in contrast to the pristine Pd cathode showing a null result.
- The Pd/SWCNT/Pd cathode in-situ gives a statistically significant result just in one 5- days electrolysis run.
- The results (in particular, the absence of electrolyte penetration and CR-39 surface damage as well as coincidence of track diameters with those obtained in dry experiments) also show that a new sample/detector- holder assembly tested in the electrolysis runs provides a suitable technique for charged particle detection during in-situ electrolysis experiments

Results on the after-electrolysis (D-desorption mode) CR-39 detection

- The charged particle emission results obtained with the Pd/SWCNT/Pd:Dx cathode after its D-loading (in exothermic D-desorption mode) show lower significance, especially for DD-reaction products (3 MeV protons).
- The results for the Pd/Re/Pd:Dx sample are similar to that obtained with the Pd/SWCNT/Pd cathode.
- Both the samples, however, show a reproducible energetic alpha emission with the two peak (11 and 15 MeV) spectra, which similar to that for the Pd/PdO:D(H) system, but differ from the alpha spectra generated by TiD_x (only one peak at E_α ~ 14 MeV).

Conclusions

- Entire results show that nanostructured composite materials deposited onto the Pd foil substrate and providing high D-loading/high D-diffusivity allow to enhance CMNS effects compared to the pristine Pd cathode during both in-situ electrolysis and exothermic D-desorption measurements.
- The charged particles detected during in-situ and after electrolysis experiments show both DD-reaction and energetic alpha particle signatures. This indicates the same origin of the CMNS effects occurred during and after electrochemical loading of the cathodes.
- The CMNS effects could be further enhanced with increase in D/C ratio (> 1.5) in SWCNTs encapsulated by thin Pd layers onto a Pd substrate.