The influence of water and carbon dioxide on lanthanide thin films produced by molecular plating

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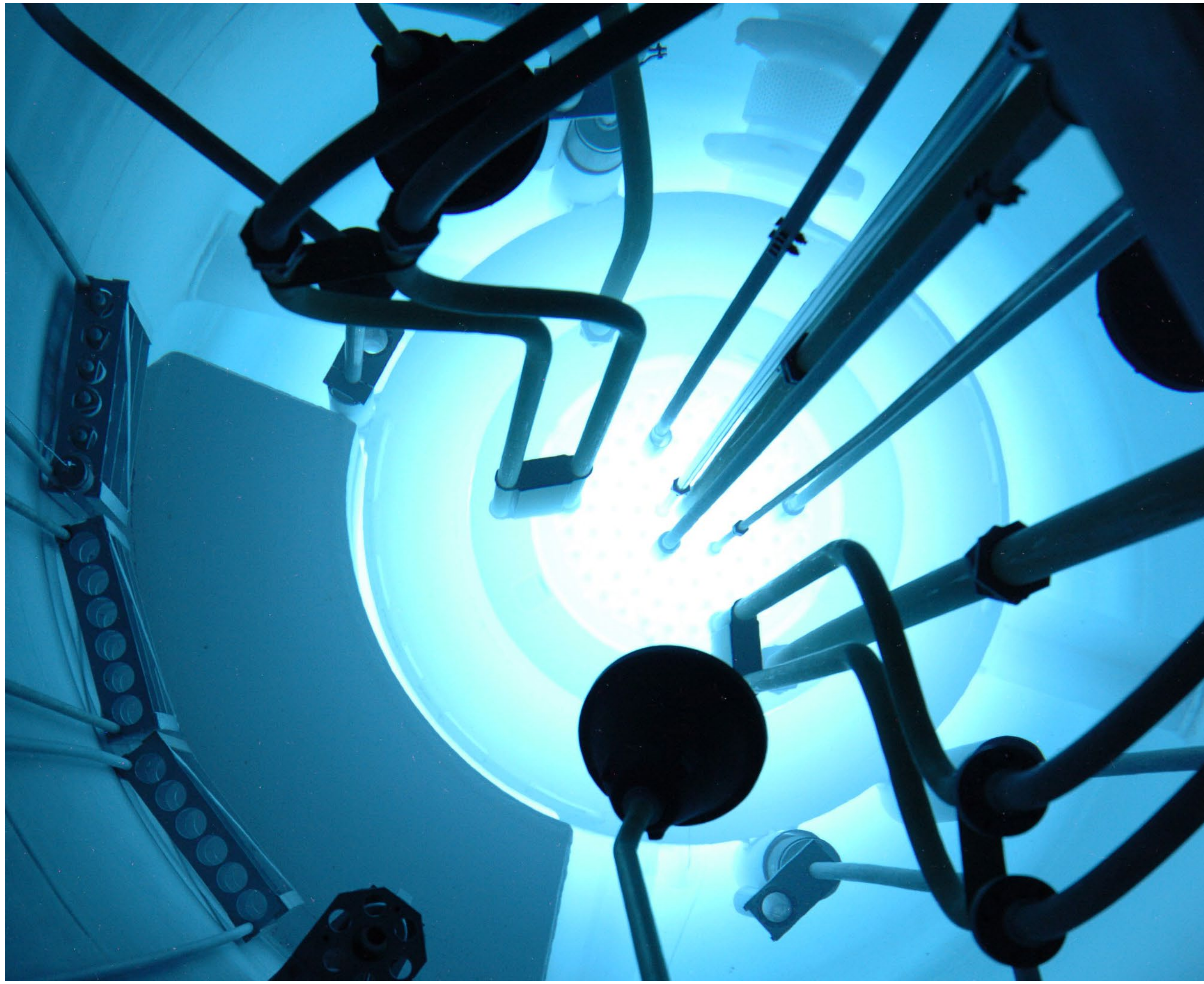


Introduction

<u>1962</u>
Molecular plating introduced

<u>1986</u>
Usage of molecular plated targets for beam experiments

<u>2012</u>
XPS analysis of MP films found carbon inside the thin film

<u>2021</u>
Confirmation of carbon compounds inside the film

<u>2022</u>
Influence of CO_2 and water on molecular plating

- Electrochemical deposition
- Organic solvents
- High yields (>90 %)
- Homogeneous layer thicknesses
- Layer thicknesses of up to 800 µg/cm^2 in a single step
- Can be used for various elements

<u>Mainly characterization of layer morphology:</u>

- **radiographic imaging (RI)**
- **atomic force microscopy (AFM)**
- **scanning electron microscopy (SEM)**

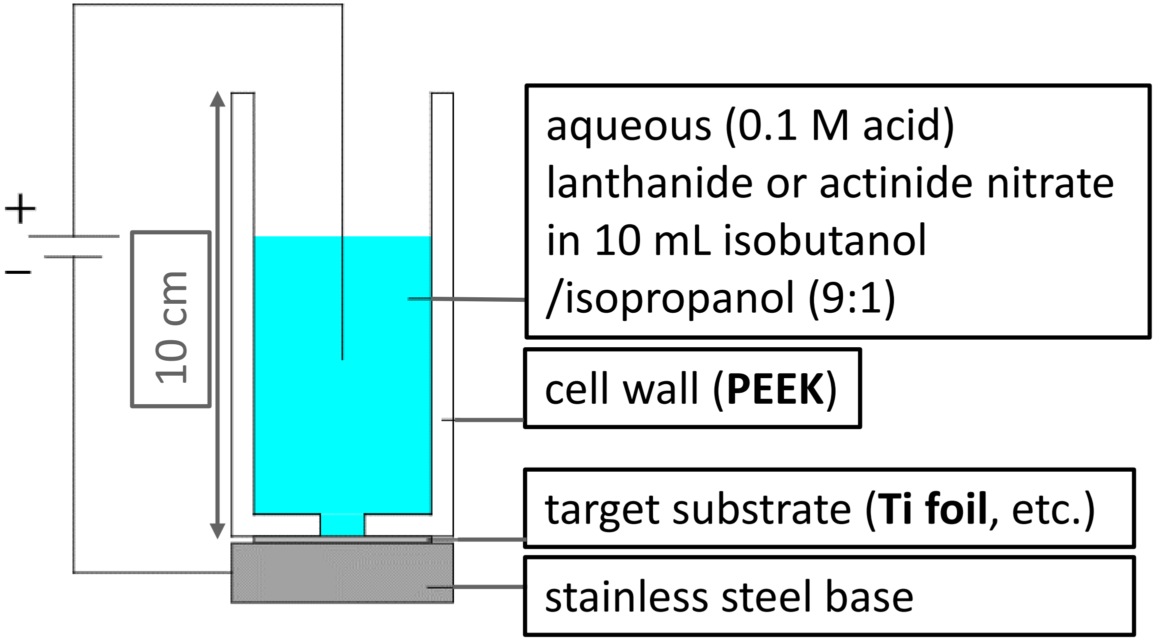
<u>Sometimes molecular plating failed without any obvious reasons!</u>

Controlled CO_2 and water amount in solution

- ➢ Use of dry solvents (< 50 ppm water)
- ➢ Work in an inert Ar atmosphere
- ➢ Terbium as a model for actinides (Z>94)
- ➢ **<u>Spectroscopic approach</u>**

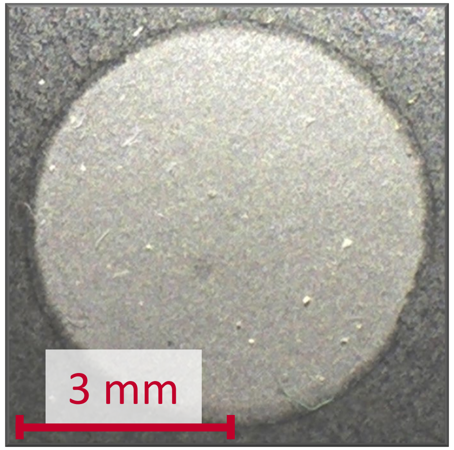
W. Parker, R. Falk, *Nucl. Instr. Meth.*, 16 (1962) 355.
B.W. Filippone, M. Wahlgren, NIM A **243** (1986) 41-44.
Vascon, A., et al., NIM A 696 (2012): 180-191.
Meyer C.-C., et al., in preparation

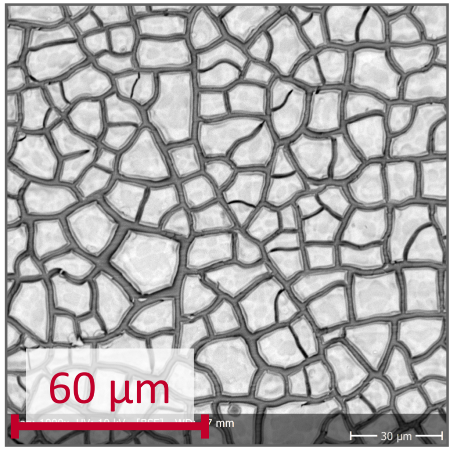
Molecular plating



high voltages: 600 – 1200 V
low current densities: 0.5-1.5 mA/cm²

Circular deposition with 6 mm diameter





Eberhardt, K., et al. *NIM A* 521 (2004): 208-213.
Loveland, W. *J. Radioanal. Nucl. Chem.* 307 (2016): 1591-1594.
Eberhardt, K., et al. *AIP Conf. Proc.* 1962, 030009 (2018).

Experimental approach

Solvent:
- Dry isobutanol and isopropanol (<50 ppm water)
- Ratio 9:1 (IB:IP)

Stock solution:
- Terbium nitrate ($Tb(NO_3)_3$) as a model for actinides (Z>94)
- Dissolved in the solvent
- No acids used

Inert atmosphere:
- Work in an Ar atmosphere
- Preparation and reaction were done inside the glovebox

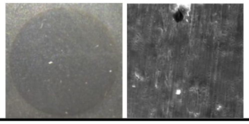
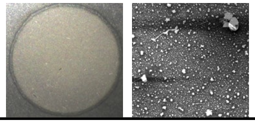
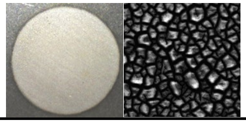
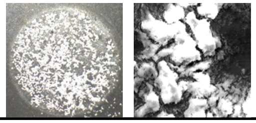
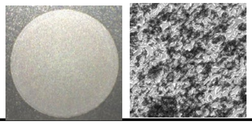
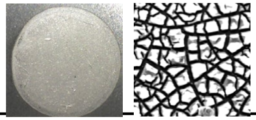
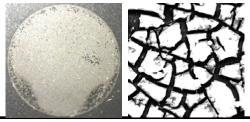
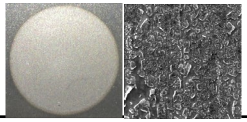
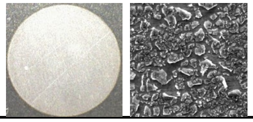
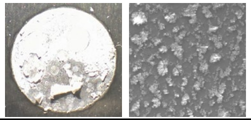
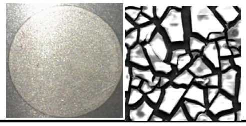
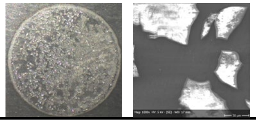
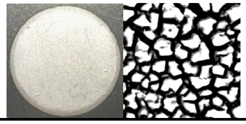
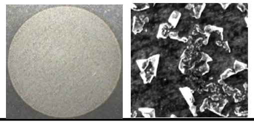
Water content:
- H_2O was substituted with D_2O for possible NMR-studies
- D_2O was added to reaction solution in different concentrations

Reaction solution:
- 142 µg Tb **(→ 500 µg/cm²)**
- 0-150 µL D_2O **(0-1.5 vol-%)**
- CO_2-saturated solvent 0-10 mL **(0-100 % saturation)**
- Filled up to 10 mL with CO_2-free solvent
- Inside the glovebox
- Deposition on Ti-foils

CO_2 introduction:
- CO_2-gas introduced to solvent
- CO_2-concentration at maximum saturation: **0.17 mol/L**
- Concentration variable by mixing CO_2-saturated solvent with CO_2-free solvent

Fogg, P. G. T., *Solubility Data Series Vol. 50 Carbon dioxide in non-aqueous solvents at pressure less than 200 kPa*, 1st Edition, Oxford, 1992.

Sample list

D_2O-concentration in vol-% / CO_2-saturation in sat.-%	0	0.5	1	1.5
0				
20				
50				
60				
80				
100				

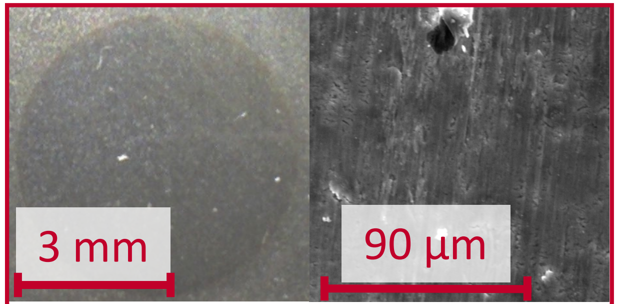
Morphology and yield:

- Light microscopy
- Scanning electron microscopy (SEM)
- Neutron activation analysis (NAA)

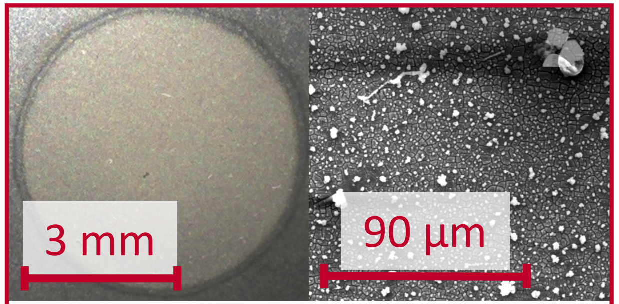
Spectroscopic methods:

- Infrared microscopy (IR)
- Confocal raman mircoscopy (Raman)

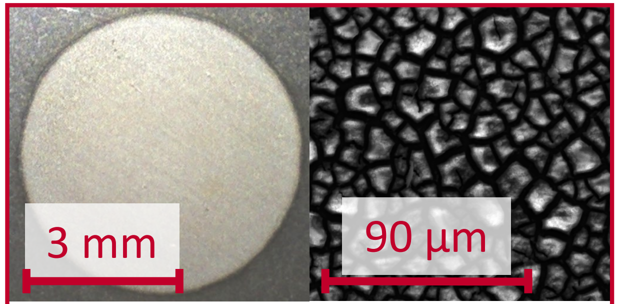
Individual influence of D_2O and CO_2



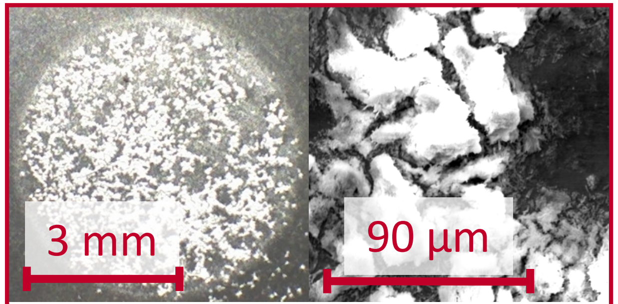
D_2O: 0 vol-%
CO_2: 0 sat.-%
Yield: 8 %
Areal weight: 40 µg/cm^2



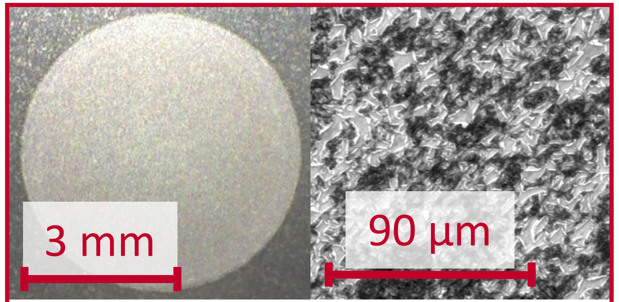
D_2O: 0.5 vol-%
CO_2: 0 sat.-%
Yield: 87 %
Areal weight: 435 µg/cm^2



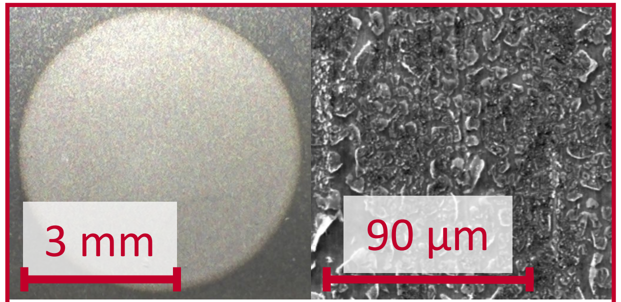
D_2O: 1 vol-%
CO_2: 0 sat.-%
Yield: 93 %
Areal weight: 465 µg/cm^2



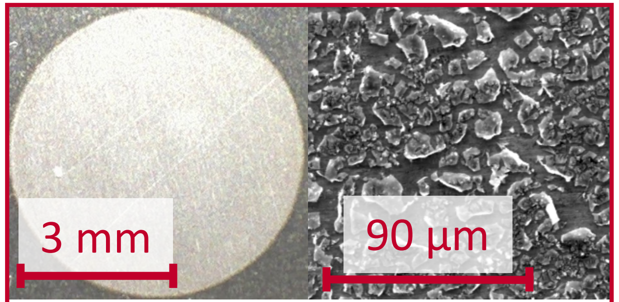
D_2O: 1.5 vol-%
CO_2: 0 sat.-%
Yield: 68 %
Areal weight: 340 µg/cm^2



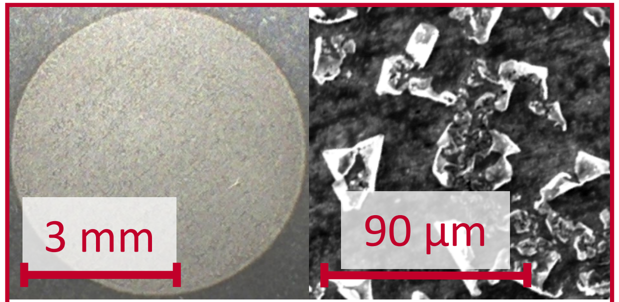
D_2O: 0 vol-%
CO_2: 20 sat.-%
Yield: 9 %
Areal weight: 45 µg/cm^2



D_2O: 0 vol-%
CO_2: 50 sat.-%
Yield: 9 %
Areal weight: 45 µg/cm^2

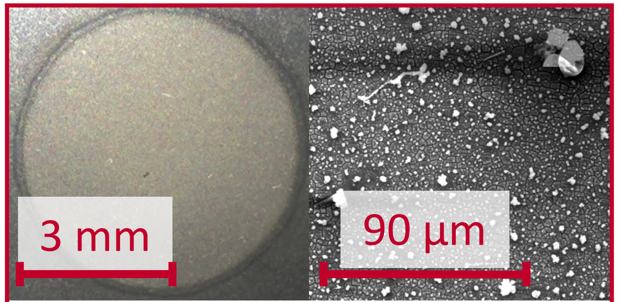


D_2O: 0 vol-%
CO_2: 80 sat.-%
Yield: 19 %
Areal weight: 95 µg/cm^2

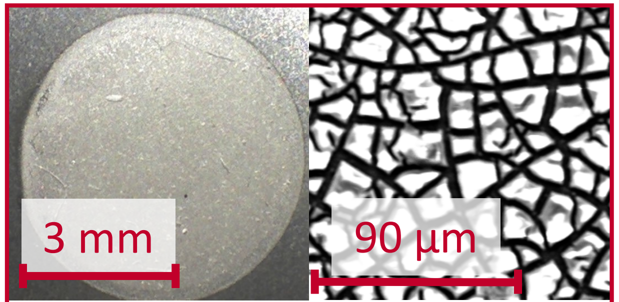


D_2O: 0 vol-%
CO_2: 100 sat.-%
Yield: 17 %
Areal weight: 85 µg/cm^2

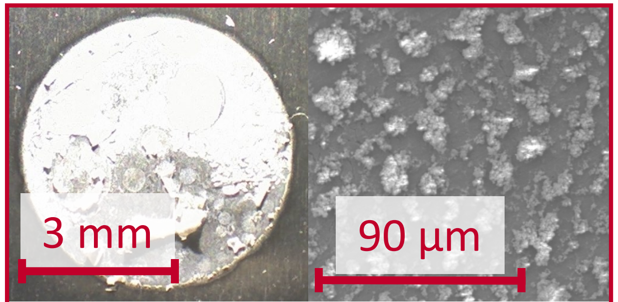
Combined influence of D_2O and CO_2



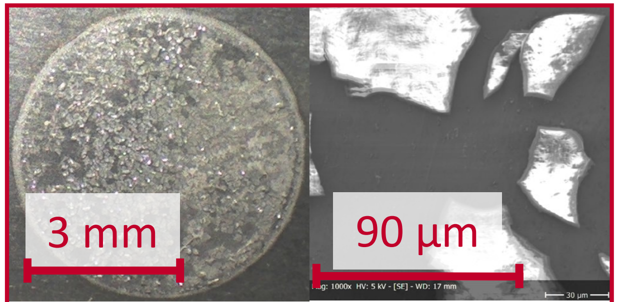
D_2O: 0.5 vol-%
CO_2: 0 sat.-%
Yield: 87 %
Areal weight: 435 µg/cm^2



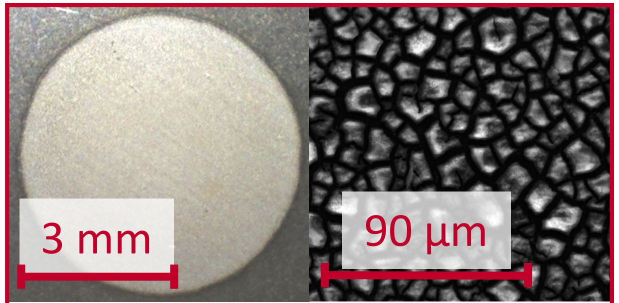
D_2O: 0.5 vol-%
CO_2: 20 sat.-%
Yield: 89 %
Areal weight: 445 µg/cm^2



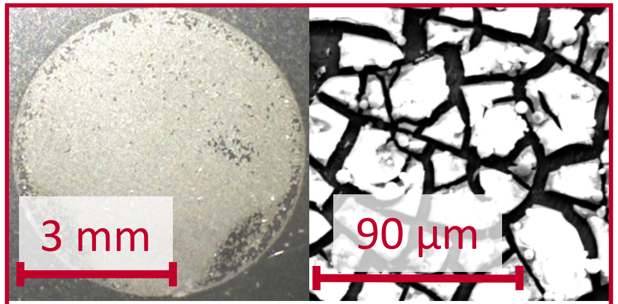
D_2O: 0.5 vol-%
CO_2: 60 sat.-%
Yield: 74 %
Areal weight: 370 µg/cm^2



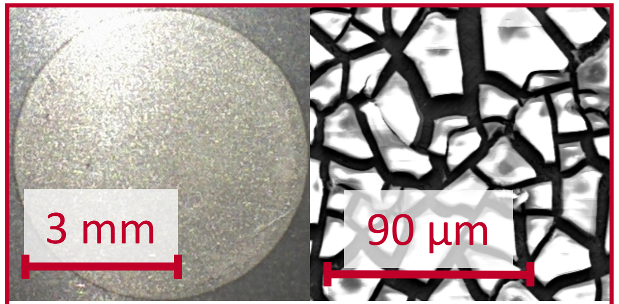
D_2O: 0.5 vol-%
CO_2: 80 sat.-%
Yield: 98 %
Areal weight: 490 µg/cm^2



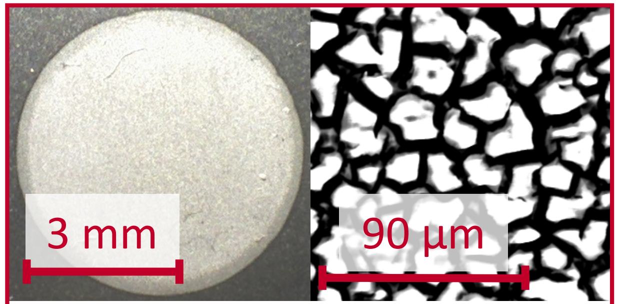
D_2O: 1 vol-%
CO_2: 0 sat.-%
Yield: 93 %
Areal weight: 465 µg/cm^2



D_2O: 1 vol-%
CO_2: 20 sat.-%
Yield: 87 %
Areal weight: 435 µg/cm^2

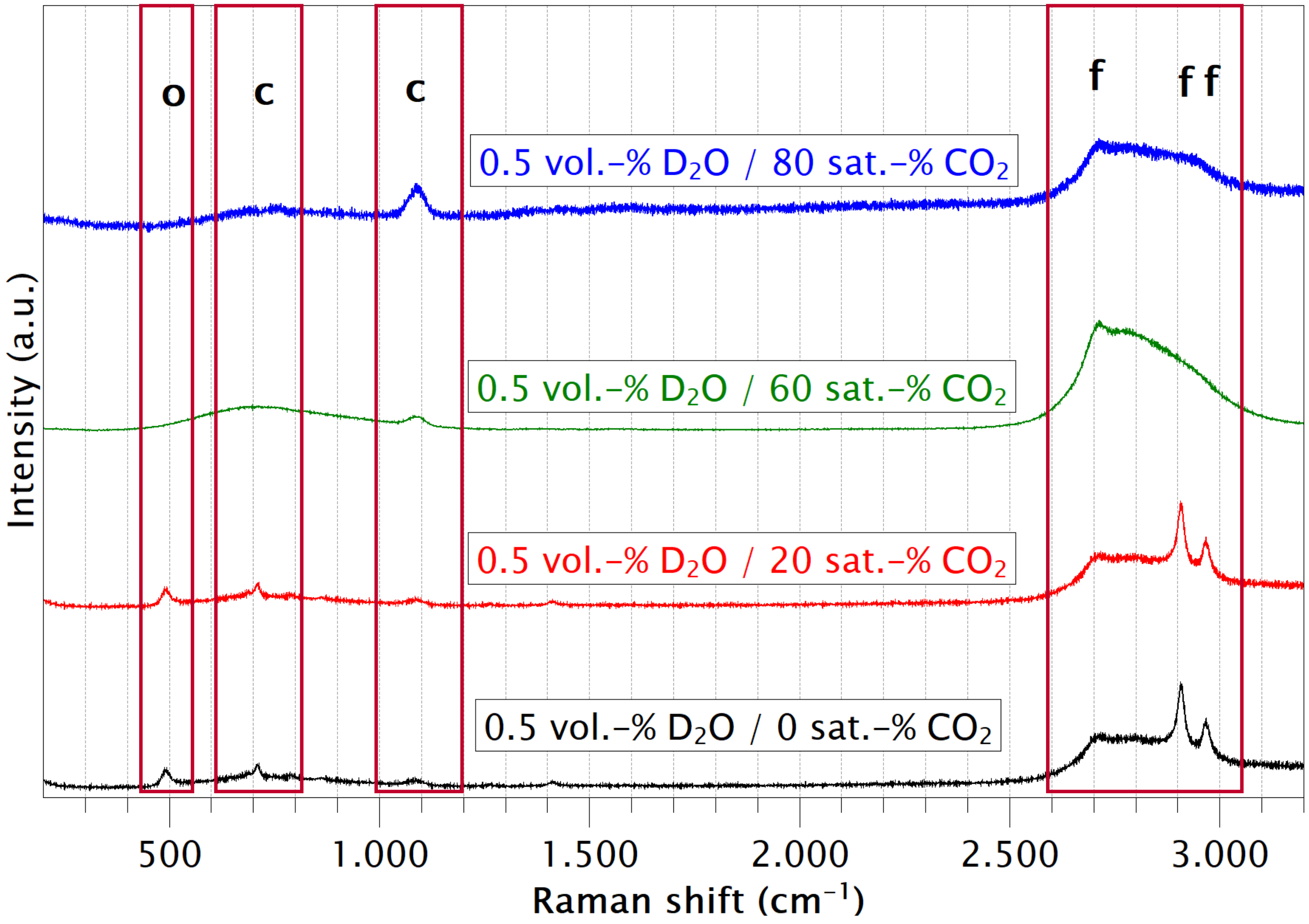


D_2O: 1 vol-%
CO_2: 60 sat.-%
Yield: 84 %
Areal weight: 420 µg/cm^2



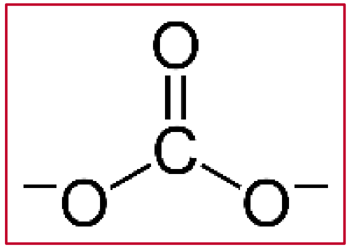
D_2O: 1 vol-%
CO_2: 80 sat.-%
Yield: 89 %
Areal weight: 445 µg/cm^2

Raman spectroscopy

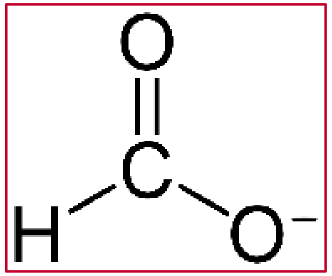


o ≡ Oxide

c ≡

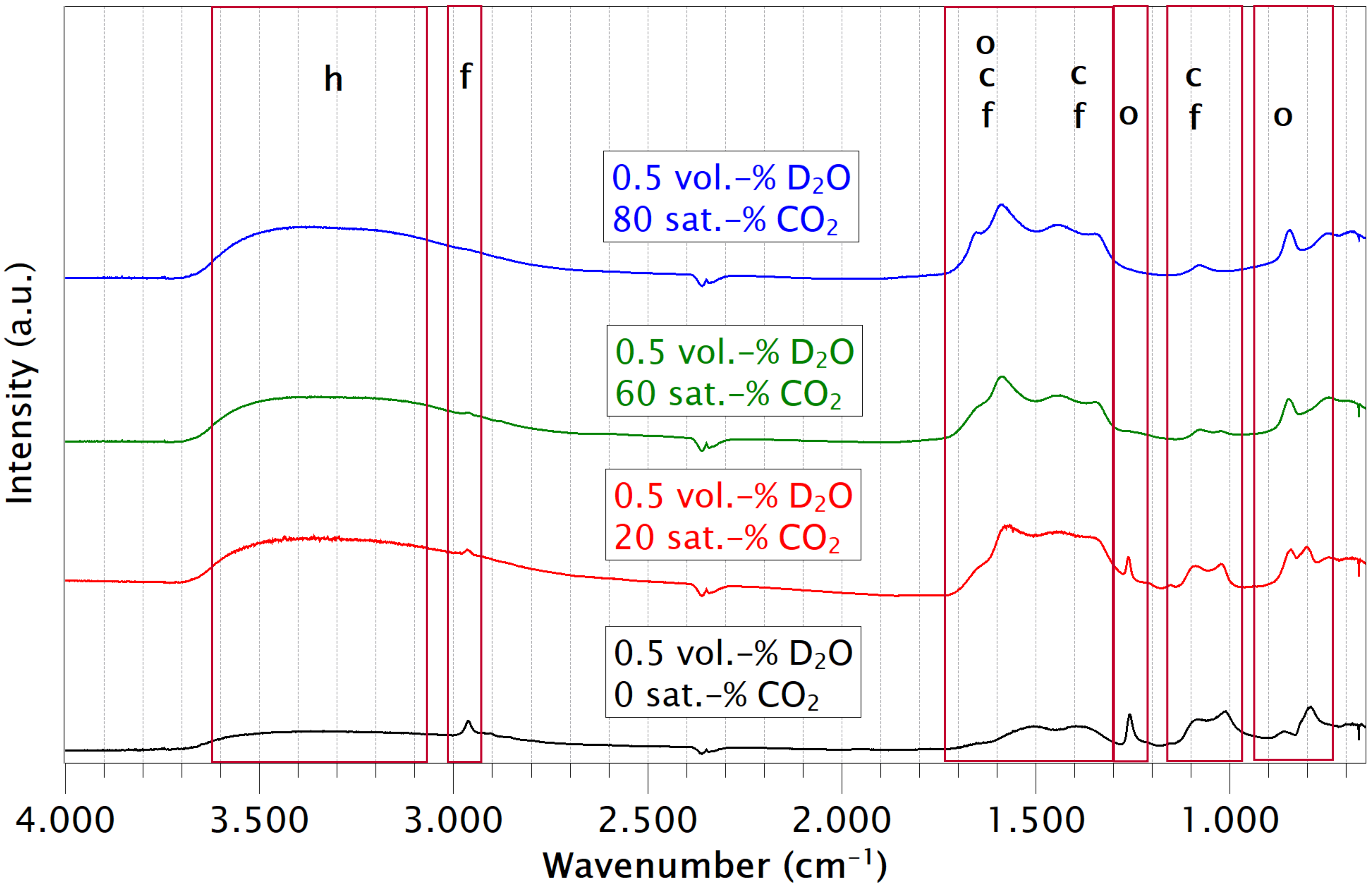


f ≡



Frost R. L., et al. *J. Raman Spectrosc. 38,* (2004): 1516-1522.
Silva, E. N., et al *J. Raman Spectrosc. 40,* (2009): 954-957.
Spiridigliozzi L., *et al J. Rare Earths 40* (2022) 1281-1290.
C.-C. Meyer et al. in preparation.

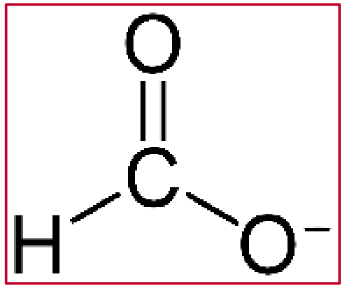
Infrared spectroscopy of the same samples



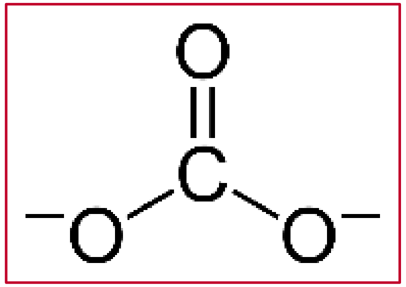
h = OH^-

o = Oxide

f =

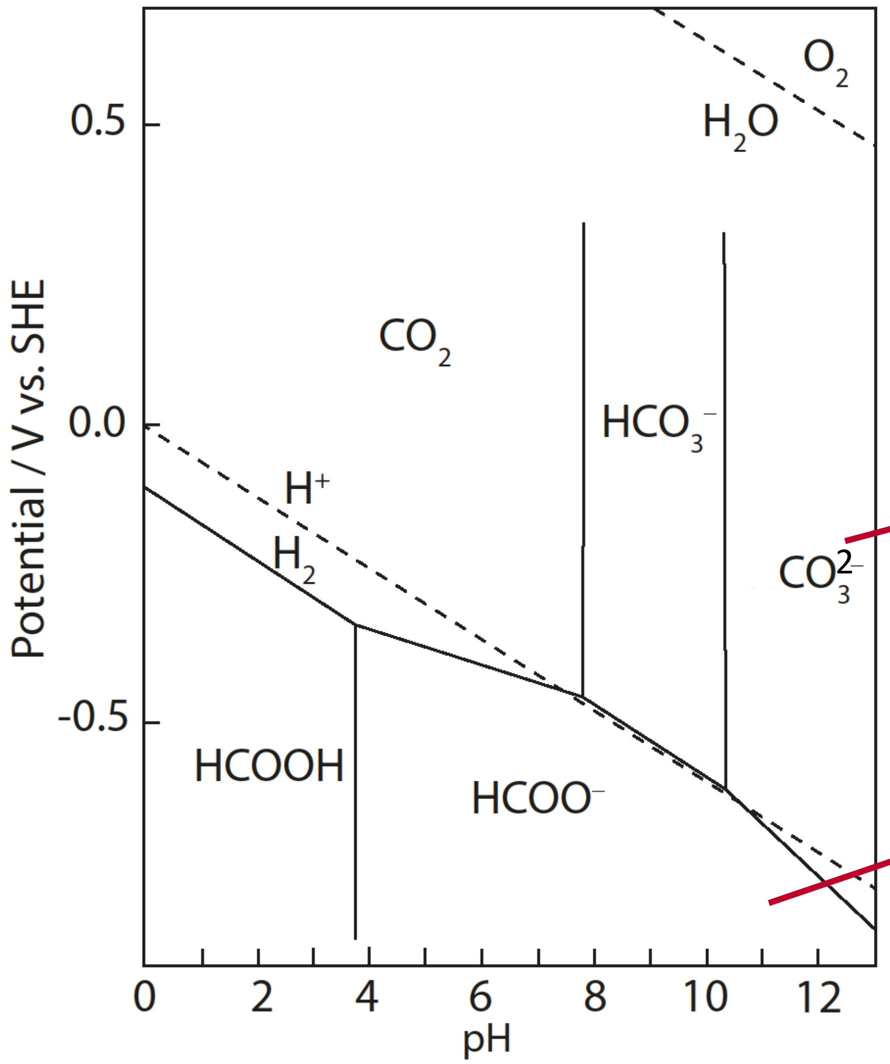


c =



Sohn, Y. *Ceram. Int. 40* (2014): 13803-13811.
Kartha, V. B., et al. *Spectrochimica Acta 37A*, (1980): 927-934.
Spiridigliozzi L., *et al J. Rare Earths 40,* (2022): 1281-1290.
C.-C. Meyer et al. in preparation

Cathode reactions



MP is a primarily hydroxide precipitaton

$$2\,H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow$$

Low potentials and locally a high pH value!

Reactions for carbonates:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$CO_2 + 2\,OH^- \rightleftharpoons {CO_3}^{2-} + H_2O$$

Reaction for formates:

$$CO_2 + H_2O + 2\,e^- \rightarrow HCOO^- + OH^-$$

Hori, Y. *Modern aspects of electrochemistry*. Springer, New York, NY, 2008.
Izutsu, K. *Electrochemistry in nonaqueous solutions*. John Wiley & Sons, 2009.
Hansen, P. *J. Inorg. Nucl. Chem.* 12.1-2 (1959): 30-37.
König, M. et al. *iScience* 19, (2019): 135-160.

Summary

- The presence of water is necessary for molecular plating
- With high water content (>1 vol.-%) films become more brittle
- The addition of CO_2 leads to a deterioration of the film quality
- Raman and IR-spectra show the presence of formates and carbonates in addition to oxides and hydroxides in the deposited film.

Best results with **0.5 – 1 vol.-% water** and **without CO_2** in the solution!