

Ex-situ Tests on Long Term Stability of Bipolar Plates for High Temperature PEM Fuel Cells

Nadine Pilinski, Henrike Schmies, Thorsten Hickmann, Peter Wagner

30.06.2021

EFCF 2021: Low-Temp. Fuel Cells, Electrolysers & H2 Processing

DLR Institute of Technical Thermodynamics

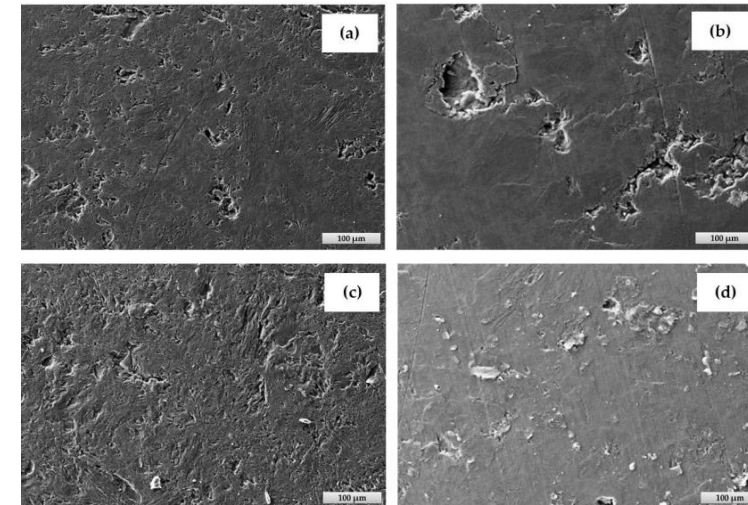


Wissen für Morgen



Bipolar Plates for High Temperature PEM Fuel Cells

- BPPs are one of the key components of HT-PEMFC
 - Degradation of BPP affects cell performance
 - Functions in a fuel cell stack
 - Feeding fuel and oxidant gases through the flow field
 - Heat transfer
 - Physical separation of FCs in series
 - Collection and transport of electrons from anode to cathode
 - Requirements of BPP
 - Electrical conductivity
 - High mechanical, electrical, thermal and electrochemical stability, ...
- ➔ Importance of materials' stability on performance of PEM fuel cells
- ➔ Limited number of studies and implemented **ex-situ tests** regarding stability of graphite-composite BPPs



SEM images of BPPs in corrosion (a) set-up A and (b) set-up B, and BPPs after electrochemical aging in (c) set-up A and (d) set-up B.

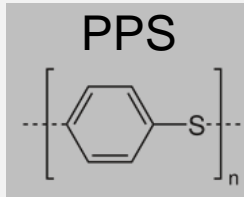
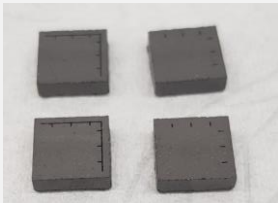
Pilinski, N.; Käding, C.; Dushina, A.; Hickmann, T.; Dyck, A.; Wagner, P. Investigation of Corrosion Methods for Bipolar Plates for High Temperature Polymer Electrolyte Membrane Fuel Cell Application. *Energies* 2020, 13, 235.



Materials and Experimental Setup

Materials

- PPS based composite BPP
=> PPS1, PPS2, PPS3



Ex-situ aging test

1. step ante-mortem

- μ -CT
- confocal microscopy
- SEM-EDS
- AFM

2. step storage test

- 85 % H_3PO_4
- 160 °C
- ~4,000 h



3. step post-mortem

- μ -CT
- confocal microscopy
- XPS
- SEM-EDS
- titration

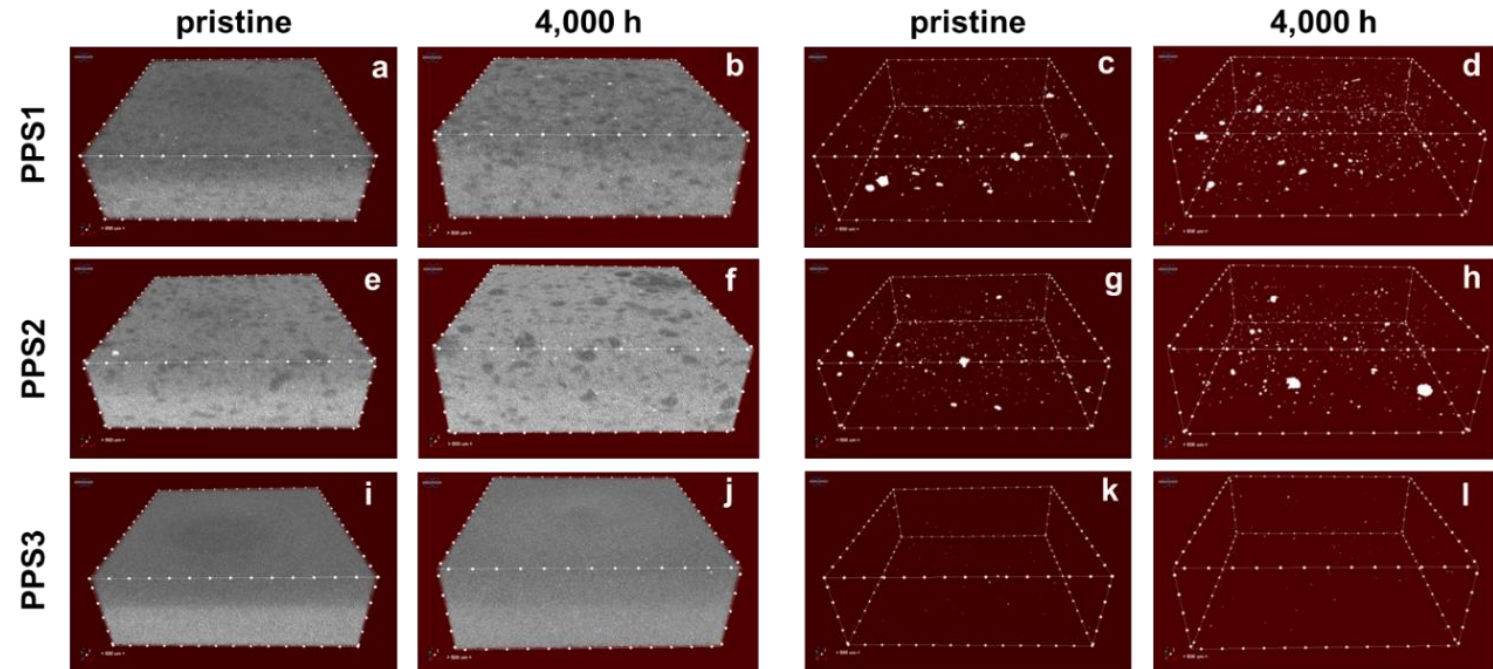
Output

- Influence of H_3PO_4 and temperature on BPP composite materials
- Determination of e.g. surface roughness, morphological changes, current distribution, acid uptake



Morphology Changes in Bulk Material with μ -CT

- Comparable morphologies for PPS1 and PPS2
- The number and size and distribution of filler particles are similar
- In the case of the PPS3, much more homogeneous material with smaller particles
- No changes in bulk material after storage in H_3PO_4

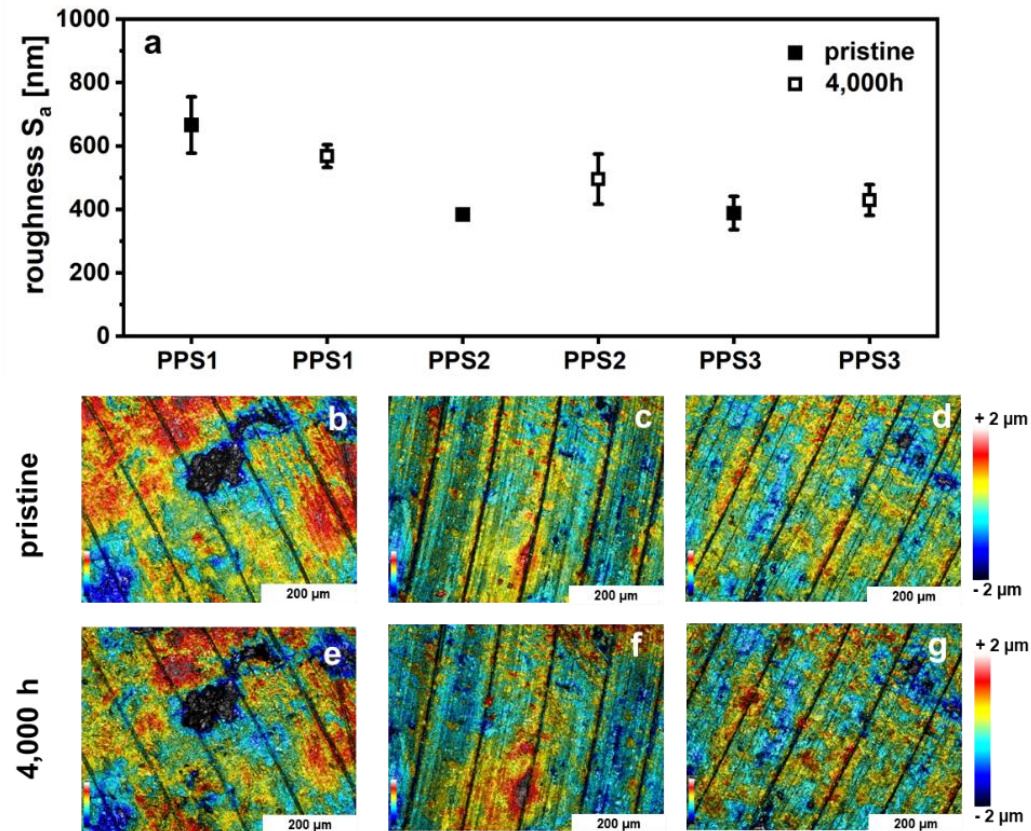


Reconstructed μ -CT images of PPS1, PPS2 and PPS3 before (pristine) and after storage for 4,000 hours in concentrated phosphoric acid at 160 °C (4,000 h) each with full illustration (a, b, e, f, i, j) and display of particles (c, d, g, h, k, l)

➔ Material changes take place on the surface of the bipolar plate



Morphology Changes on Surface Area with Confocal Microscopy



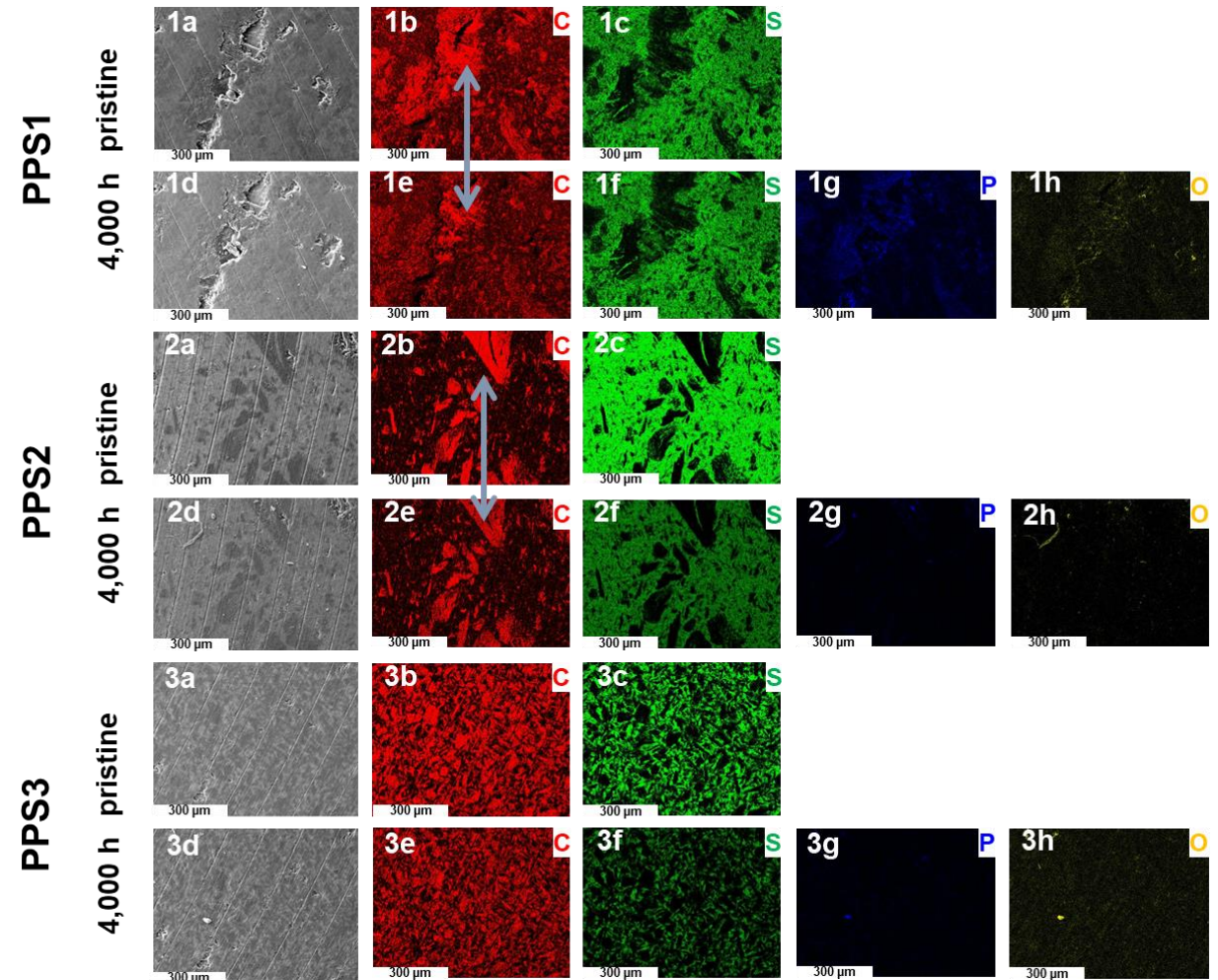
Comparison of roughness S_a (a) and 2D images of PPS1 (b, e), PPS2 (c, f) and PPS3 (d, g) before (b-d) and after 4,000 hours (e-g) measured with confocal microscopy

- Roughness of PPS1 (600 to 900 nm) slightly higher compared to PPS2 and PPS3 (400 to 500 μm) before and after stress test
 - Wider and higher graphite particle size distribution adapted in PPS1 resulting in more inhomogeneous surface
- Similar surface area of PPS2 and PPS3
 - In contrast to analysis of bulk material: PPS1 ~ PPS2
- Negligible effect of acid and temperature to the surface area regarding PPS1, but negative impact to PPS2 and PPS3 with slightly higher roughness



Morphology Changes on Surface Area and Material Composition with SEM

- PPS1 and PPS2 with higher inhomogeneity of elements compared to PPS3
 - Significantly larger graphite particles in the material in PPS1 and PPS2 detected by μ -CT
- No serious changes in the surface before and after storage
- Slight decrease of carbon content
- Phosphorus and oxygen as residues of phosphoric acid from the storage



SEM images und EDS element distribution (carbon, C; sulfur, S; phosphorus, P; oxygen, O) of PPS1 (1a-h), PPS2 (2a-h) and PPS3 (3a-h) before and after storage for 4,000 hours in concentrated phosphoric acid at 160 °C

Analysis of Elements with SEM-EDS

- Elemental distribution of carbon, sulphur, phosphorus and oxygen in wt% of PPS1, PPS2 and PPS3

		C / wt%	S / wt%	P / wt%	O / wt%
PPS1	pristine	93.9	6.0	-	-
	4,000 h	88.6	6.4	1.7	3.4
PPS2	pristine	87.0	13.0	-	-
	4,000 h	76.9	7.6	1.9	13.6
PPS3	pristine	94.9	4.9	-	-
	4,000 h	86.4	4.3	1.9	7.5

- Reduction in carbon content after storage for all samples
- Sulphur content of PPS2 is significantly reduced after storage and constant in the case of the PPS1 and PPS3

- ➔ Higher polymer content (sulphur in polyphenylene sulphide) might lead to oxidation of sulphur in addition to corrosion of carbon?
- ➔ This is further confirmed by a higher oxygen content after 4,000 hours at the surface

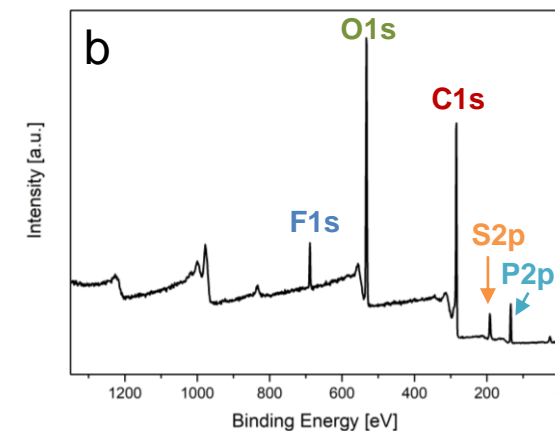
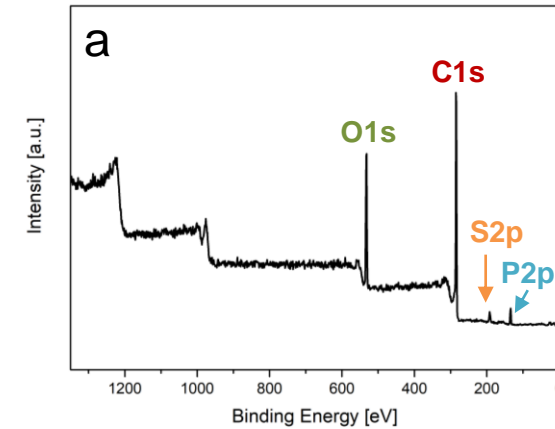


Elemental Composition with XPS

- Surface composition from quantitative analysis of the XPS survey spectra of PPS1 and PPS3 after storage

	C / at%	O / at%	S / at%	P / at%	F / at%
PPS1	78.9	17.4	-	3.7	-
PPS3	55.2	34.1	0.2	6.9	3.4

- F signal could also be detected on the surface of PPS3
 - Dissolution of a certain amount of PTFE from the Teflon vessels during storage
- Less carbon and higher amount of oxygen on surface of PPS3
 - In good agreement with EDS analysis
 - Partly due to local inhomogeneities



XPS survey spectra of (a) PPS1 and (b) PPS3 after storage for 4,000 hours in concentrated phosphoric acid at 160 °C

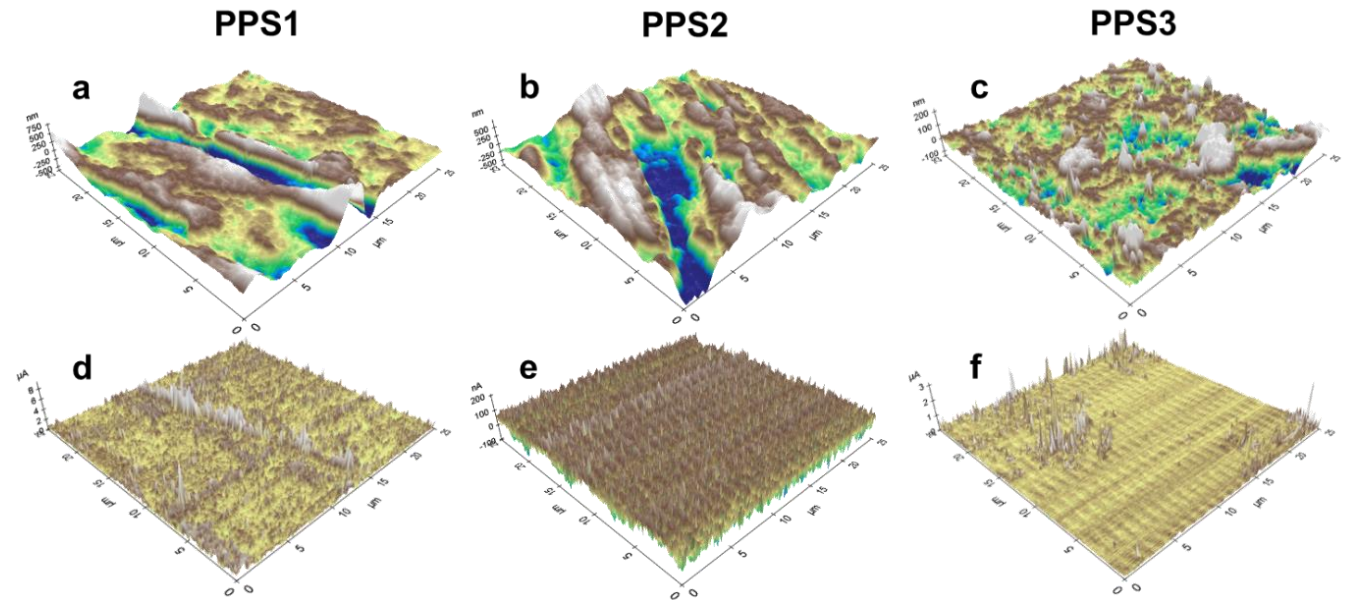
Surface Area and Electrical Properties with Conductive AFM

• Topography

- Comparable surface and roughness of PPS1 and PPS2
- Significantly less roughness of PPS3

• Local current distribution

- PPS1: homogeneous current distribution with locally high currents of up to $10\ \mu\text{A}$
- PPS2: no currents above the noise level of about $100\ \text{nA}$
 - higher proportion of non-conductive PPS
- PPS3: currents are significantly lower with a maximum of $3\ \mu\text{A}$, large local differences in the current distribution

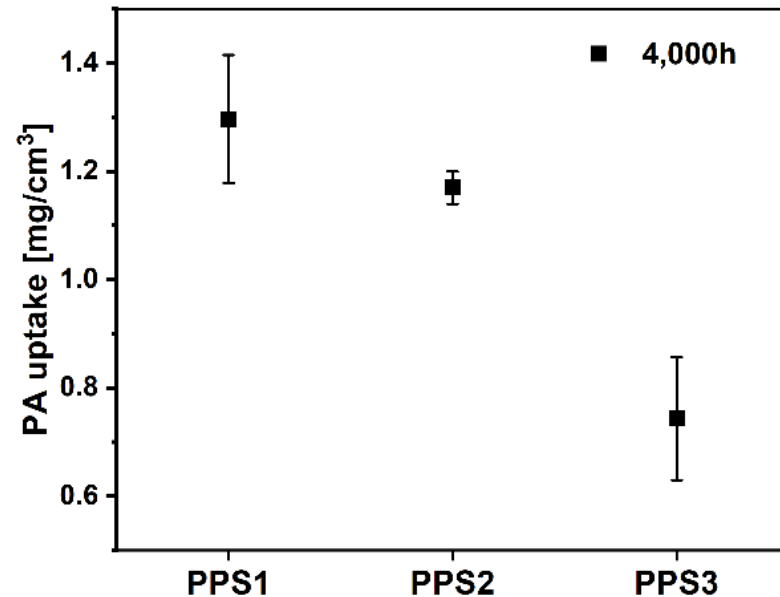


3D images of topography and local current distribution at $1.0\ \text{V}$ for PPS1 (a, d), PPS2 (b, e) and PPS3 (c, f) measured by C-AFM; area: $25 \times 25\ \mu\text{m}$. The topographies as well as the current distributions at a voltage of $1.0\ \text{V}$ are displayed



Acid Uptake with Titration Method

- Phosphoric acid uptake of PPS1, PPS2 and PPS3 determined by titration



Phosphoric acid uptake in mg/cm³ of PPS1, PPS2 and PPS3 after 4,000 hours determined by titration with sodium hydroxide

- Highest uptake of phosphoric acid with PPS1 (~1.3 mg/cm³)
- Slightly lower values of PPS2 with 1.2 mg/cm³
 - Wider and higher graphite particle size distribution and lower amount of graphite compared to PPS1
- PPS3 significantly lower with a factor of two (0.7 mg/cm³)
 - Lower contact of phosphoric acid and less penetration into the material due to the more homogenous morphology and smooth surface

➔ Effect of particle size and homogeneity on uptake of acid



Conclusions

- Ex-situ tests in phosphoric acid at 160 °C for 4,000 h on three PPS based composite BPP materials for HT-PEM fuel cell application
- Ante- and post-mortem analysis with μ -CT, confocal microscopy, SEM-EDS, XPS, AFM and titration
- Impact of material composition and homogeneity on morphology, content of carbon and sulphur, electrical properties and phosphoric acid uptake

➔ Suitable ex-situ method to simulate HT-PEMFC application

1. step: ante-mortem analysis

μ -CT, confocal microscopy, SEM-EDS, C-AFM

2. step: storage test for 4,000 hours

concentrated H_3PO_4 , 160 °C

3. step: post-mortem analysis

μ -CT, confocal microscopy, XPS, SEM-EDS, titration



Acknowledgements

The authors would like to thank the German Federal Ministry of Transport and Digital Infrastructure for funding the German project InProPlate (03B11008B2)

Supported by:



Coordinated by:



Thank you for attention!

Questions?

- **Contact:**

E-Mail: Nadine.Pilinski@DLR.de

Phone: +49 441 99906-314

Website: www.DLR.de

