# HySTor: Development of Novel In-Situ Silica Sol-Gel Barrier Coatings for Mitigating Hydrogen Permeation

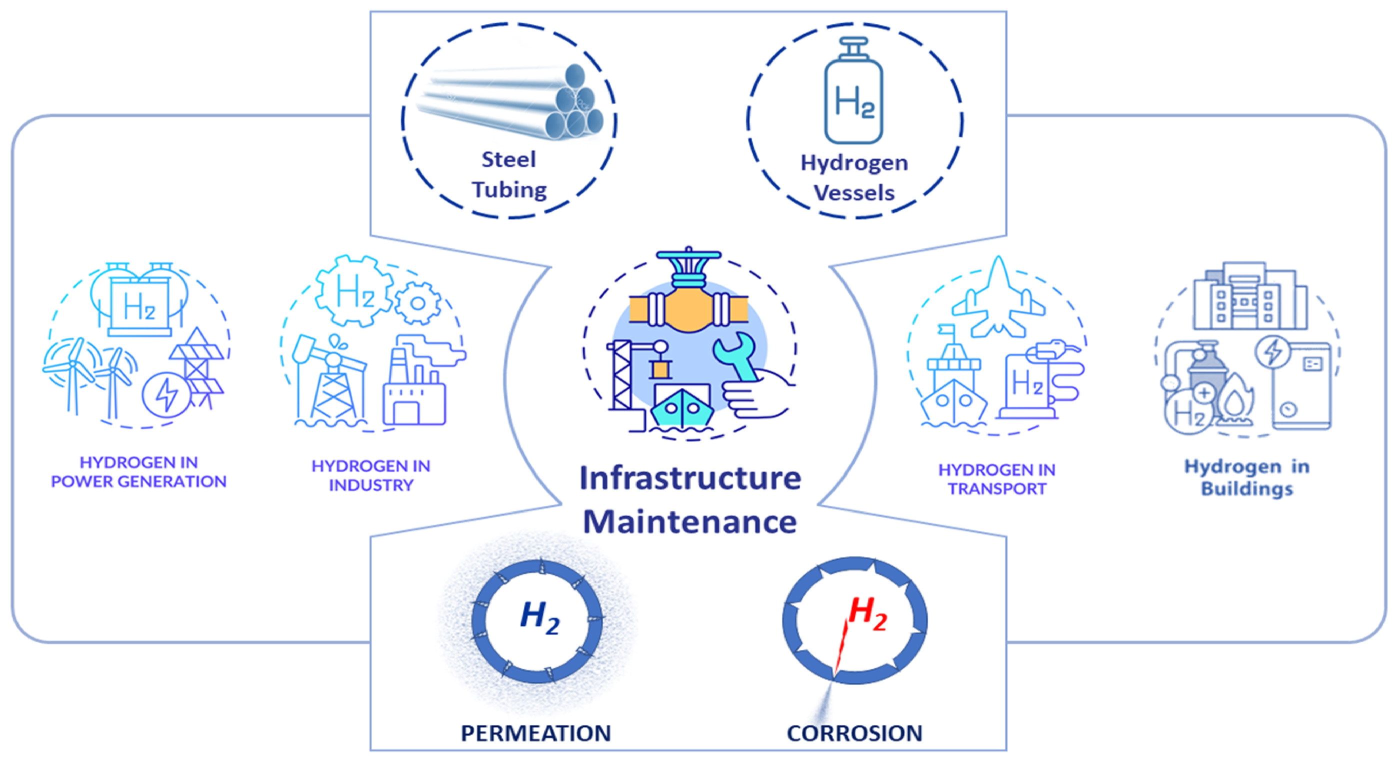
Natalia Kaczmarczyk [1], Michal Ozga [2], Anna Szczurek [3], Bartosz Babiarczuk [1], Beata Borak [1], Przemyslaw Wiewiórski [1], Pawel Gasior [1], Jerzy Kaleta [1], Walis Jones [1,4], Justyna Krzak [1*]

[1] Department of Mechanics, Materials and Biomedical Engineering, Wroclaw University of Science and Technology, Wroclaw, Poland; [2] Faculty of Chemistry, Wroclaw University of Science and Technology, Wroclaw, Poland; [3] FN-CNR CSMFO Lab. and FBK Photonics Unit, Povo, Italy; [4] BioPharm Enterprises Limited, 65 Gwaun Afan, Cwmafan, Port Talbot, UK; * *corresponding author: justyna.krzak@pwr.edu.pl*

## BACKGROUND

With the emerging focus of Hydrogen as a fuel in the Green Economy, there is an urgent need to deliver solutions related to the safe and efficient storage and transmission of Hydrogen. Two critical areas related to both cost efficiency and safety relate to the highly permeable and corrosive properties of Hydrogen molecules as a gas. One area of focus is the formation of barrier coatings to limit both hydrogen permeation and the reduction of its corrosive effects upon the underlying substrate of the storage vessel material. While the formation of barrier coatings as part of the production process of the storage vessels and piping is the primary goal, a secondary goal is to apply such protective coatings in situ within existing infrastructure, such as storage vessels and existing pipelines.

This project focus on the synthesis and application of novel sol-gel coating materials based on Silica as a flexible approach to deposit Silica network multilayers as cost-effective barrier coatings. As part of this approach, the process of sol-gel maturation and understanding the forces that drive silica network development and interaction between Hydrogen and the newly-developed coated surfaces are now being studied dynamically using a range of surface-measurement instruments, including surface plasmon resonance (SPR).




## METHODS AND RESULTS

Two hydrolysates based on Ethyltriethoxy silane - EtEOS (2A) and *n*-Propyltriethoxysilane - *n*-PtEOS (3C), were studied. The molecules of both precursors and the structure of resulting networks are depicted in Figures 1 and 2. The hydrolysates were mixed for 2 hours at room temperature, after which they were aged for 24 hours prior to applying on gold sensors. The sensors were coated with 3 layers of respective hydrolysate via dip-coating method. Coated sensors were stabilised in an oven for 3 hours at 40°C followed by 12 hours at 90°C. Sensors were analysed in an SPR-Navi 200L multi-parametric surface plasmon resonance (MP-SPR) instrument (Bionavis). The data was analysed via the LayerSolver software program (Bionavis).

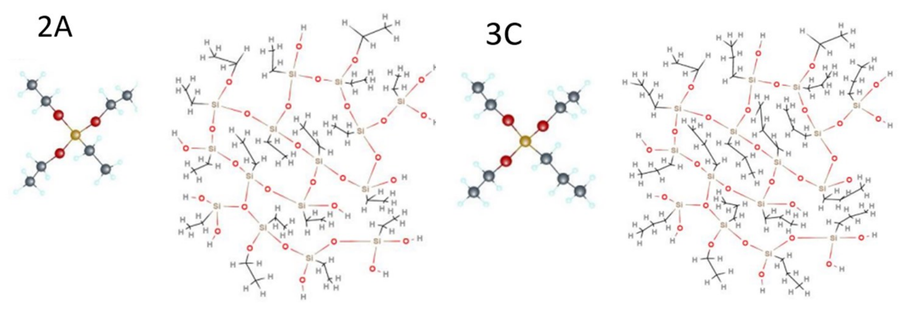



FIGURE 1. Graphical representations of the Silica-Oxide matrices formed by the two precursor hydrolysates, namely, EtEOS] - 2A) and n-PtEOS - (3C).

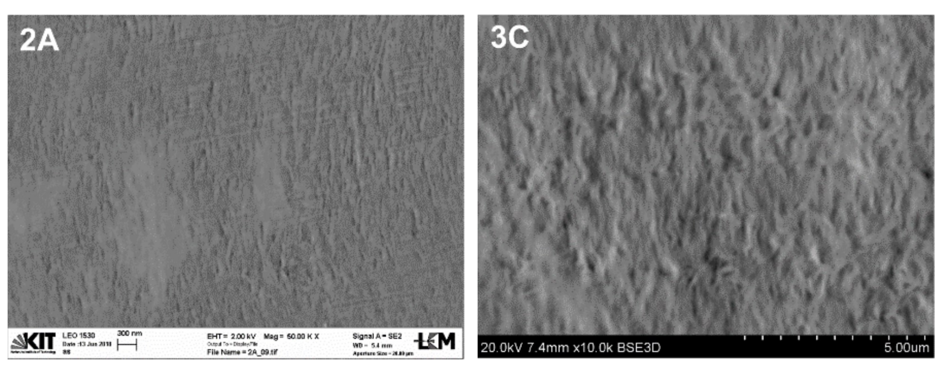
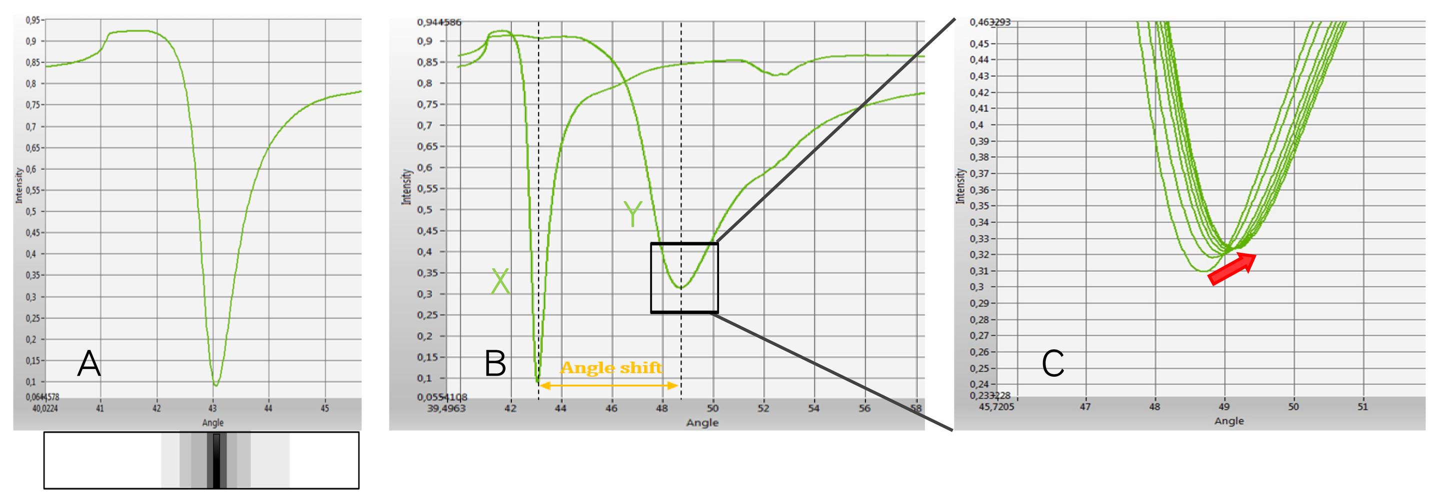
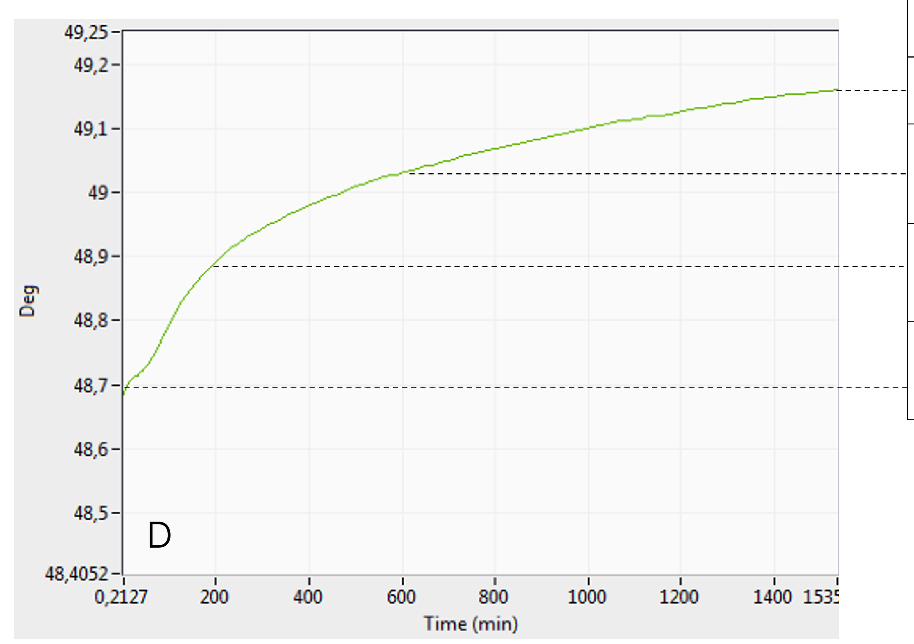



FIGURE 2. Images showing layers of hydrolysates 2A and 3C applied to High-Density Polyethylene [HDPE]




| Thickness [nm] | Refractive Index (Real value) | Refractive Index (Imaginary value) |
|---|---|---|
| 57,99 | 1,30137 | 0,03278 |
| 55,06 | 1,32952 | 0,03810 |
| 48,96 | 1,36375 | 0,04375 |
| 39,15 | 1,46039 | 0,05802 |

FIGURE 3. A. Typical SPR-Curve of gold sensor slide in air, showing the drop in Intensity at the Peak Minimum Angle (PMA) at approximately 43°. B. Shift in resonance angle between a gold sensor slide in air (X) and a gold sensor slide coated with a silica-oxide coating (Y). C. Gradual change in the PMI of the silica-oxide coating over time, accompanied by a continual decrease in Peak Minimum Intensity (PMI). D. Sensorgram representation of PMA changes shown in (C).

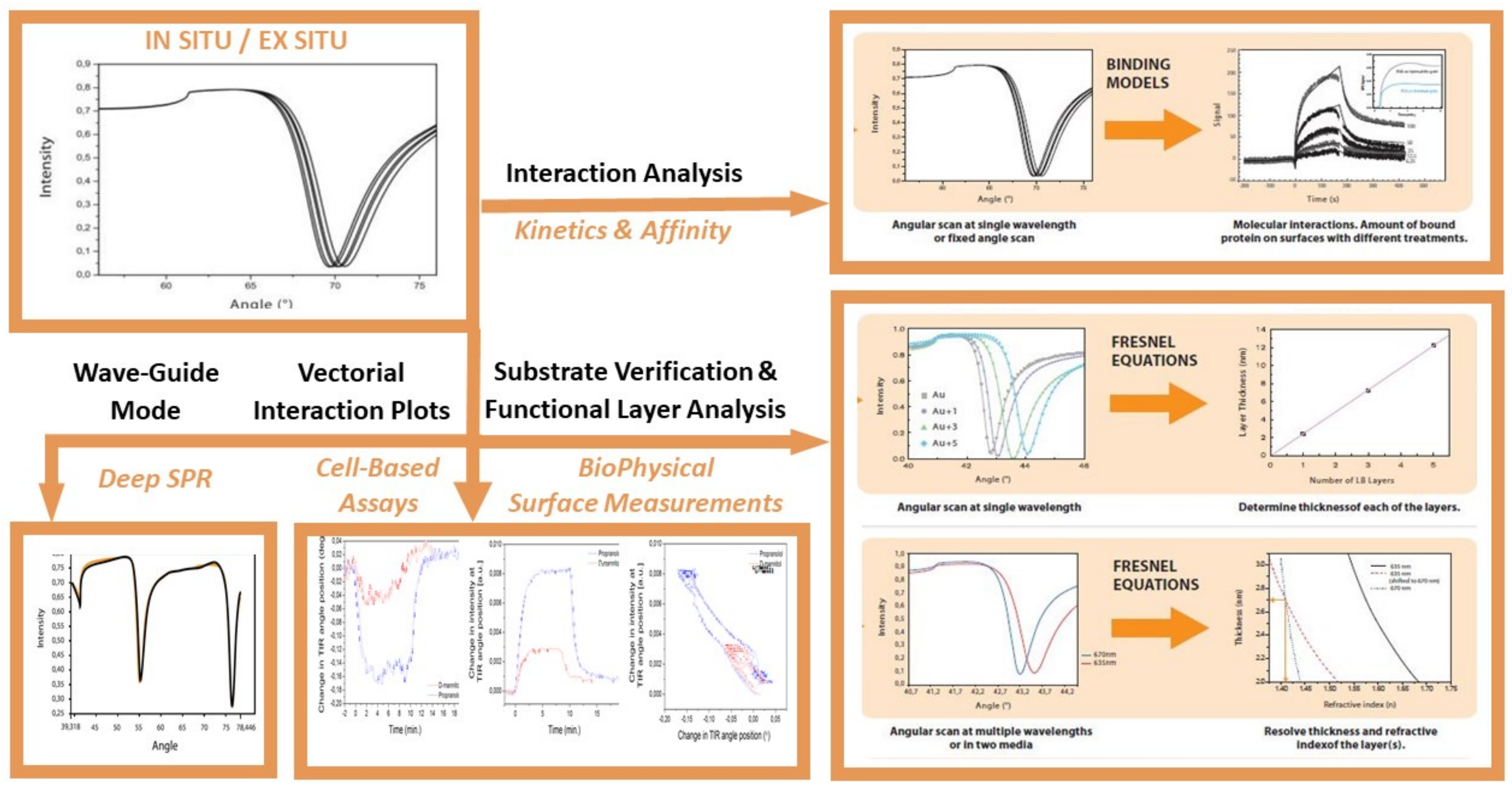
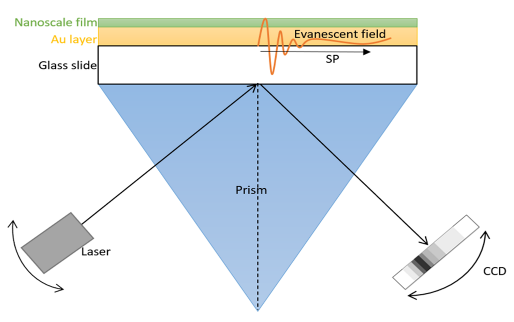



FIGURE 4. Applications of the Reflectance Spectrum or SPR-Curve for Dynamic Physical Measurements of Surface Layers

Conventional surface plasmon resonance (SPR) analysis is based upon a sensorgram of Angular Change extracted from a Reflectance Spectrum or SPR-Curve (Top left-hand panel). This is widely used in biology and drug discovery for establishing kinetic parameters of biomolecular interactions (Top right-hand panel). However, it is possible to extract much more information from the SPR-Curve, as shown in the three lower panels. Since the Reflectance Spectrum represents optical phenomena occurring at the sensor surface, the same data can also be analysed via mathematical approaches based upon Maxwell's Equations and Fresnel Equations for Reflection and Transmission.

This more advanced level of data analysis and interpretation can be used for substrate verification and functional layer analysis and provide further information concerning changes in layer thickness and layer density and changes in mass that occurs at the surface (Lower right-hand panel). Such surface measurements can provide information related to conformational change within the matrix of the surface layer, with a potential resolution of changes in surface layer thickness down to approximately one Angstrom. Further applications of the Maxwell and Fresnel Equations enable the analysis of thick layers that behave in wave-guide mode (Lower left-hand panel), including Dynamic Mass Redistribution (Lower middle panel).




Fresnel Equations for p-polarised light

$$r_p = \frac{n_2 \cos\theta_i - n_1 \cos\theta_t}{n_1 \cos\theta_t + n_2 \cos\theta_i}$$

$$t_p = \frac{2n_1 \cos\theta_i}{n_1 \cos\theta_t + n_2 \cos\theta_i}$$

FIGURE 5. Kretschman Configuration of SPR

Surface plasmon resonance occurs when electrons are excited by photons of light striking at a certain incident angle at the interface of two different media separated by a thin metallic layer. The maximum of excitement is characterised by a reduced intensity of the reflected light and is dependent upon the relative refractive index between the two materials. The plasmon resonance propagates parallel to the metal surface as an evanescent field, which is sensitive to any changes that occur at the interface, such as a new surface coating.

The data can be interpreted using the Fresnel equations, as summarised in the lower-left hand panel, where $r_p$ is the reflectance, $t_p$ is the transmittance or refreaction, *n1* and *n2* are the respective refractive index of each medium, respectively, and $\cos\theta_i$ and $\cos\theta_t$ represent the incident angle and transmitted angle, respectively.

Changes in the SPR-Curve can therefore be analysed via the Fresnel concerning changes in the overlying surface layer, such as the silica-oxide coatings being studied in this project.

## DISCUSSION

- Analysis of SPR data should be able to provide an indication of the following performance parameters of the silica-oxide coatings:
- Changes in the nature of aging of the silica-oxide network itself over time
- Specific effect of curing parameters and conditions on silica-oxide performance and aging
- Correlation of specific optical parameters at the nano-level with structure morphology at the micro-level, with the aim of achieving 'optical fingerprints' characteristic of specific structural conditions
- Rate of Hydrogen gas adsorption to the silica-oxide layer
- Rate of Hydrogen gas release from the silica-oxide layer
- This increased level of understanding of the mechanism of silica-oxide network formation and progression will provide a tool that can be used to monitor and control the process, thereby defining the process and the nature of the silica-oxide network itself. In this way, it is hoped that 'designer' silica-oxide coatings will be achievable, with process control enabling the production of coatings with specific performance characteristics and functionality.

## SUMMARY AND CONCLUSIONS

These studies demonstrate the feasibility of using surface plasmon resonance (SPR) as a measurement tool for monitoring the chemical process of silica-oxide sol-gel formation and aging. It further illustrates the sensitivity of SPR in being able to monitor Hydrogen gas adsorption and release from porous silica-oxide matrices and that different matrices show differential barrier properties to Hydrogen gas. Future directions of the project are aimed at establishing the relationship between specific SPR optical outputs with specific morphological silica-oxide structures, with the aim of being able to control the synthetic process to deliver surface coatings with defined micro structure and function.

## LITERATURE

- Sadowski, J., Method for Carrying Out Surface Plasmon Resonance Measurement and Sensor for Use in the Method. June 21, 1994, Patent US005322798A
- Anna Szczurek, RozprawaDoktorska (PhD Thesis) Modyfikacja materiałów polimerowych z zastosowaniem powlok tlenkowych otrzymywanych metoda zol-zel w celu ograniczenia przenikalnosci gazów. (2021), Wroclaw University of Science and Technology, Poland.

## ACKNOWLEDGEMENTS

The research was supported by the National Center for Research and Development in Poland under the Small Grant Scheme (SGS) project 'Improving the Efficiency of Hydrogen Storage Vessels through Novel Oxide Coatings HyStor NOR/SGS/HyStor/0306/2020-00' Programme 'Applied Research' financed through the Norwegian Financial Mechanism.

For further information, please visit: