

# Characterising the Sticking Coefficient of Chemistries Relevant for Artificial Solid Electrolyte Interphases

Léo Lapeyre<sup>a</sup>, Krzysztof Mackosz<sup>a</sup>, Wojciech Szmyt<sup>a,b</sup>, Laszlo Pethö<sup>a</sup>, Johann Michler<sup>a</sup>, Patrice Raynaud<sup>c</sup>, Ivo Utke<sup>a</sup>

<sup>a</sup> Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland.

<sup>b</sup> EPFL, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

<sup>c</sup> LAPLACE, Laboratoire Plasma et Conversion d'Energie, CNRS, Toulouse, France.

## Motivation

- With the increasing demand for longer life time and safer batteries, atomic layer deposition (ALD) has become the method of choice for the synthesis of artificial solid electrolyte interfaces [1-3] (SEIs) due to its outstanding thickness control and conformality of deposited films, allowing the surface treatment of porous cathode active material (CAM) from batteries electrodes in a unique way.
- Aiming for the full coverage of the active material, ALD process must be optimized in order for precursors to diffuse in the porous 3D structures of CAMs.
- To this end, high aspect ratio (AR) porous Si structures were employed to determine the penetration depth of precursors and characterise 1) the sticking probability and 2) the ALD regime (reaction- or diffusion-limited) of various chemistries relevant for artificial SEIs.

## ALD regimes and diffusion-reaction model

Szmyt et al. (2022) [4] developed a set of scaling laws describing the different ALD regimes (reaction- or diffusion-limited) and their corresponding surface coverage with respect to coating depth and sticking probability. Eq. (1) shows the expression of the coverage in the diffusion-limited regime, i.e. the dominating regime when depositing on high AR and porous substrates, as represented on Fig.1.

$$\theta(t) = \frac{\lambda_c}{L} \sqrt{\frac{J\beta_0}{n_0}} t \quad (1)$$

With  $\theta$  - the surface coverage,  $\lambda_c$  - the reaction front width,  $L$  - total length of the pores,  $n_0$  - the substrate surface sites density,  $J$  - the flux of molecules to surface,  $\beta_0$  - the sticking coefficient and  $t$  - the time.

The diffusion-limited regime allows to calculate the sticking coefficient of precursors, by determining the reaction front width  $\lambda_c$  through the coverage profile of the chemisorbed film:

$$\lambda_c = \frac{4}{\bar{s}} \sqrt{\frac{2}{3\beta_0}} \quad (2)$$

Where  $\bar{s}$  is the surface area to void volume ratio of the structure where precursors diffuse.

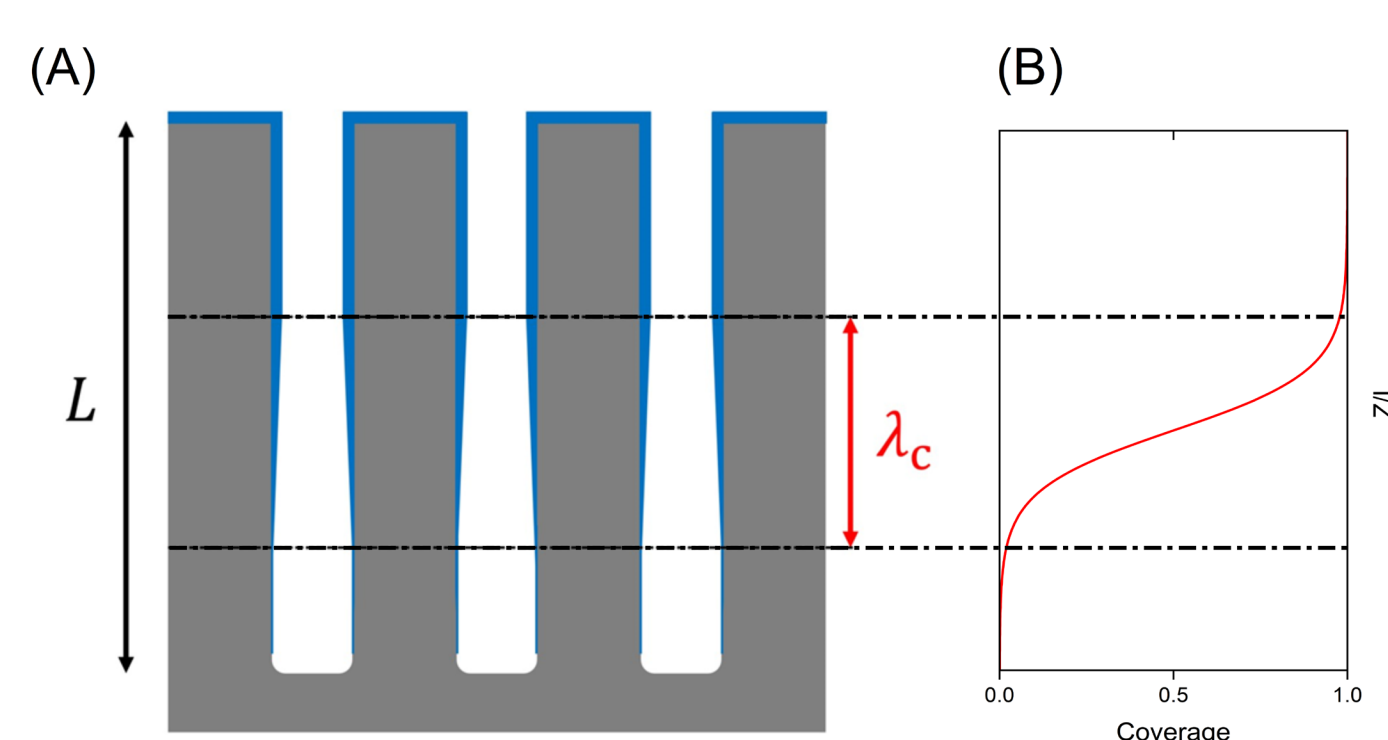


Figure 1. (A) Illustration of diffusion-limited ALD regime taking place in porous high AR Si and (B) associated coverage profile. Blue color represents the chemisorption coverage.

- In our work, we apply this model to porous Si structures (series of cylindrical holes, see Fig. 1), allowing to determine the penetration depth of the coating inside the pores. The reaction front width, and therefore, the sticking coefficient of precursors can be obtained. From this value, information on the behaviour of a given ALD precursors are gathered, such as its diffusivity, deposition regime or ability to provide conformal coatings in high AR.
- Finally, this study aims to define the optimized ALD parameters (such as precursor exposure time or butterfly valve opening) for maximizing the penetration depth of precursors inside porous structures and apply such parameters for the surface treatment of cathode active materials (CAM) employed in batteries.

## High AR porous Si chip

The substrates employed in this investigating are home-made porous Si chips (1x1 cm<sup>2</sup>) synthesized by photolithography. The pores are defined by a 3 μm opening and a 100 μm depth, providing an AR of 30. The pores density is 1.25 × 10<sup>4</sup> cm<sup>2</sup>.

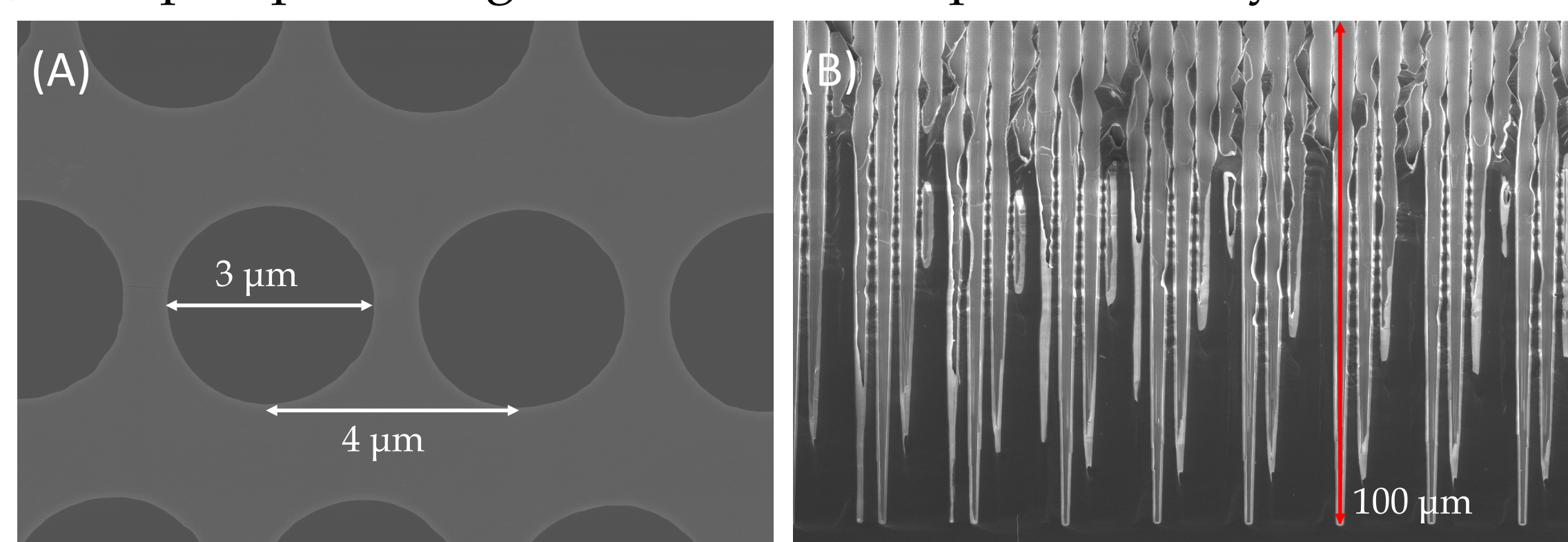


Figure 2. SEM images of (A) Top view and (B) cross-section view of high AR porous Si substrate for diffusivity and sticking coefficient investigation.

The dimensions of the pores were chosen to present similar AR as the porous cathode active material substrates, to be coated for the end-application of the artificial SEIs.

## References

- [1] Ma et al., "Atomic Layer Deposition for Lithium-Based Batteries" Adv. Mater. Interfaces, 2016, 3, 1600564; DOI: 10.1002/admi.201600564
- [2] Wang et al., "Electrochemical investigation of an artificial solid electrolyte interface for improving the cycle-ability of lithium ion batteries using an atomic layer deposition on a graphite electrode", Journal of Power Sources, 2013, 233, 1-5; DOI: 10.1016/j.jpowsour.2013.01.134
- [3] Gao et al., "Ionic conductive polymers as artificial solid electrolyte interphase films in Li metal batteries – A review Materials Today, 2020, 40, 140-159; DOI: 10.1016/j.mattod.2020.06.011
- [4] Szmyt et al., "Atomic Layer Deposition on Porous Substrates: From General Formulation to Fibrous Substrates and Scaling Laws Chem. Mater. 2022, 34, 203–216; DOI: 10.1021/acs.chemmater.1c03164

## Reaction front width determination

A key parameter for obtaining precise values of  $\beta_0$  is the determination of the reaction front width ( $\lambda_c$ ) of coatings inside the pores. By acquiring cross-section images with in-beam back scattered electrons (BSE) detector, the different elements are highlighted by a difference in contrast (as seen from Fig.3(A)) and the coverage profile can be numerically obtained.  $\lambda_c$  is then defined as the distance between the two 1<sup>st</sup> order derivative flipping of the coverage curve.

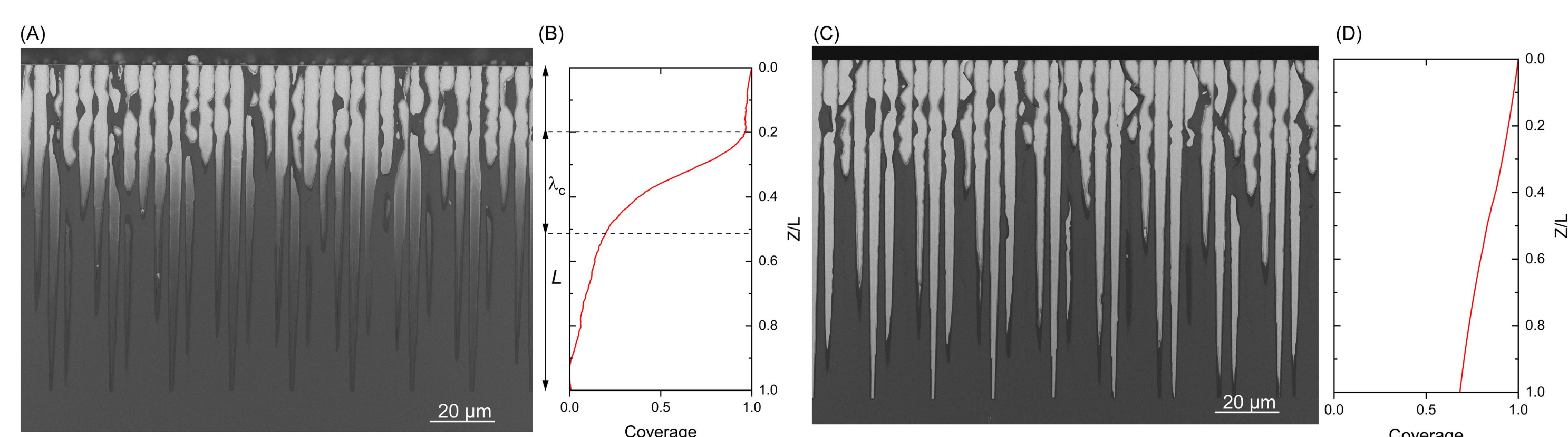


Figure 3. Cross-section SEM in-beam BSE image of porous Si coated by atomic layer deposition of SnO<sub>2</sub> with (A) 5 s exposure and (C) 30 s exposure time. (B) and (C) are the associated coverage profiles processed numerically from SEM images. The profile curve is obtained by averaging the coverage of 10 different pores.

- Additionally, this method allows to modify specific ALD process parameters (here the precursor exposure time) for optimising the coating's coverage, as seen on Fig. 3(C). In this case, the sticking coefficient can not anymore be extracted from coverage profile, as the ALD process is running in now running in the reaction-limited regime.

## Sticking probabilities

Table 1 shows the sticking coefficients obtained from our method on two different chemistries. In the current state of the work, only two precursors could be characterized.

Coating	Precursor / Co-reactant	$\beta_0$
Al <sub>2</sub> O <sub>3</sub>	TMA / H <sub>2</sub> O	$> 1.85 \times 10^{-6}$
SnO <sub>2</sub>	TDMASn / H <sub>2</sub> O	$1.5 \times 10^{-2}$

- Due to the high diffusivity of TMA, this precursor experienced a reaction-limited regime and would require higher AR to force the diffusion-limited regime and provide a precise value of  $\beta_0$ . Therefore, only a minimal value of  $\beta_0$  can be obtained for TMA.

## Conclusions

- A quick method for characterizing various precursors behavior, such as diffusion and conformality capabilities, is presented.
- In the context of high AR structures, most of precursors will present a diffusion-limited regime, giving rise to a reaction front.
- Applying the diffusion model introduced by Szmyt et al. (2022) [4] allows to determine the precursor's sticking coefficient from coverage profile vs. penetration depth.
- This characterization method will be employed on different chemistries relevant for artificial SEIs, such as LiO<sup>t</sup>Bu or Nb(OE)<sub>5</sub> with the objective of optimizing ALD process parameters for improved batteries performances.
- Porous-Si chips presenting higher AR (in the range of 100) will be synthesized in order to study a wider range of precursors, including the most diffusive ones.

