Computational Insights into the Buried Interface of Silica-Coated Pt Electrocatalysts

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Abstract

Semipermeable membranes are attractive as protective coatings for metal electrocatalysts in harsh environments, but their impact on the catalytic properties has not been fully understood. Experimentally probing buried membrane-catalyst interfaces is challenging because standard surface-science techniques cannot be directly used.

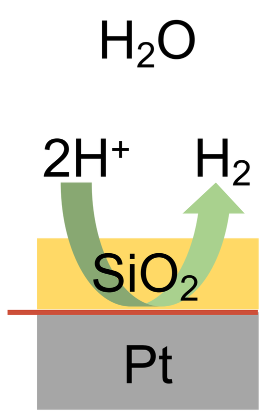
Here, we discuss insights from first-principles modeling of silica coated platinum electrocatalysts. We introduce the concept of interface *Pourbaix diagrams* to investigate the interaction of silica membranes with the surface of platinum metal electrocatalysts under different electrochemical conditions. The structure, composition, and adhesion energy of the buried SiO_2/Pt interface depend on the pH value of the aqueous electrolyte and the electrode potential. Membrane-coating also affects the electronic structure of the catalyst surface, which has direct implications for the catalytic reactivity

Our analysis indicates that semipermeable membrane coatings are not passive bystanders but affect the properties of electrocatalysts, thereby offering as yet unexplored tuning knobs for the design of corrosion-stable electrocatalysts.

[1] J. Qu and A. Urban, *ACS Appl. Mater. Interfaces* **12** (2020) 52125–52135.

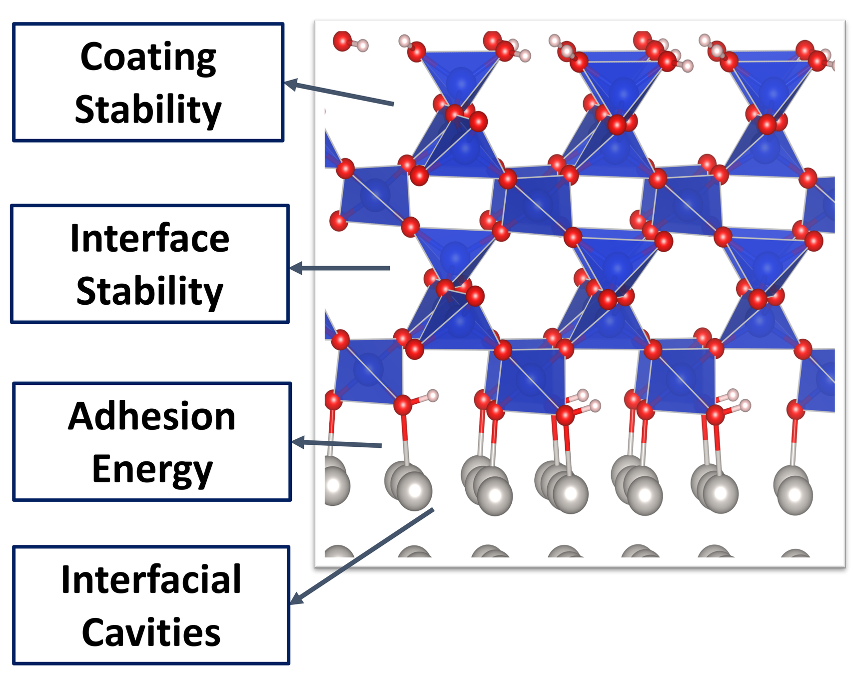
Membrane-Coated Catalysts

- Membrane-coated electrocatalysts (MCECs) are catalyst architectures in which the surface of the catalyst is coated with a semipermeable membrane.
- The coating is permeable for both reactants and products but protects the catalyst surface from poisons and from corrosion.
- Silica-coated platinum MCECs have been well characterized experimentally for hydrogen evolution reaction [2], but not much is known about the atomic structure of the buried interface.

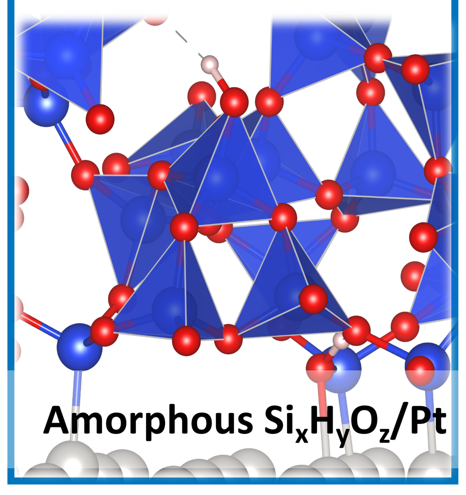


[2] D. Esposito, *ACS Catal.* **8** (2018) 457–465.

Some properties of interest for catalyst design:



Note:
The structure of the silica coating is amorphous. Transport properties depend on the structure.



Computational Approach

- We derived an approximation of the interface free energy as a function of the pH value and the electrode potential [1].
- Part of this expression is the conventional computational hydrogen electrode approximation [3].

$$\boxed{\mathrm{Pt(111)} + \mathrm{Si_6H_2O_{13}}} + (y-13)\mathrm{H_2O} + (x-2y+24)\mathrm{H^+} + (x-2y+24)e^- \rightleftharpoons \boxed{\mathrm{Si_6H_xO_y/Pt}}$$

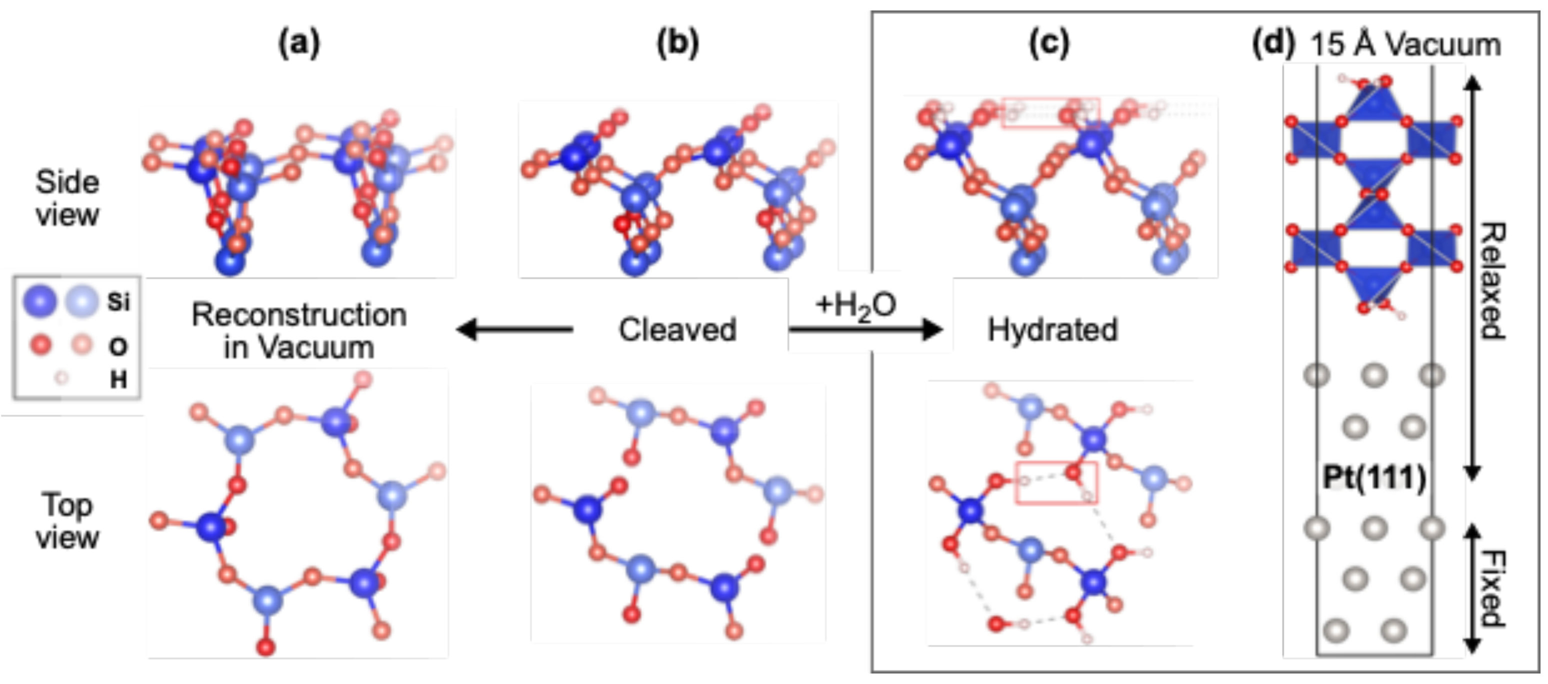
Reference models — Interface model

Formation Energy at 0 K in vacuum

$$\Delta G(\mathrm{pH}, U) \approx E_{(\mathrm{Si_6H_xO_y})/\mathrm{Pt}} - E_{\mathrm{Pt(111)}} - E_{\mathrm{Si_6H_2O_{13}}} - (y-13)E_{\mathrm{H_2O}} - (x-2y+24)\left[\frac{1}{2}\left(E_{\mathrm{H_2}} - TS^{\circ}_{\mathrm{H_2}}\right) - 2.3k_BT * \mathrm{pH} - e * U_{\mathrm{SHE}}\right]$$

T, P : 298 K, 1 atm — pH — Potential

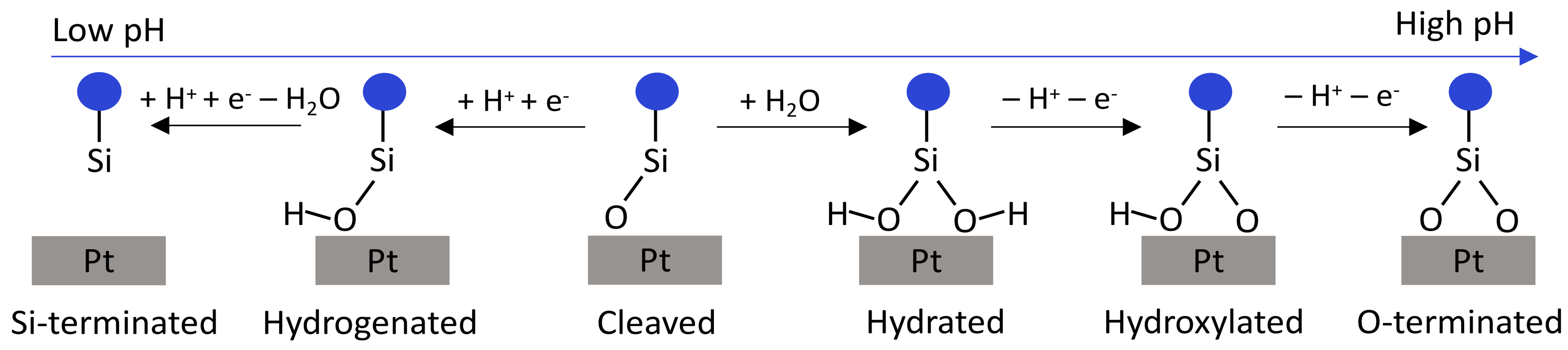
- The surface of silica forms a reconstruction in vacuum and reacts with water if present.
- We considered both surface terminations at the buried interface.



[3] J. Nørskov et al., *J Phys Chem B* **108** (2004) 17886–17892.

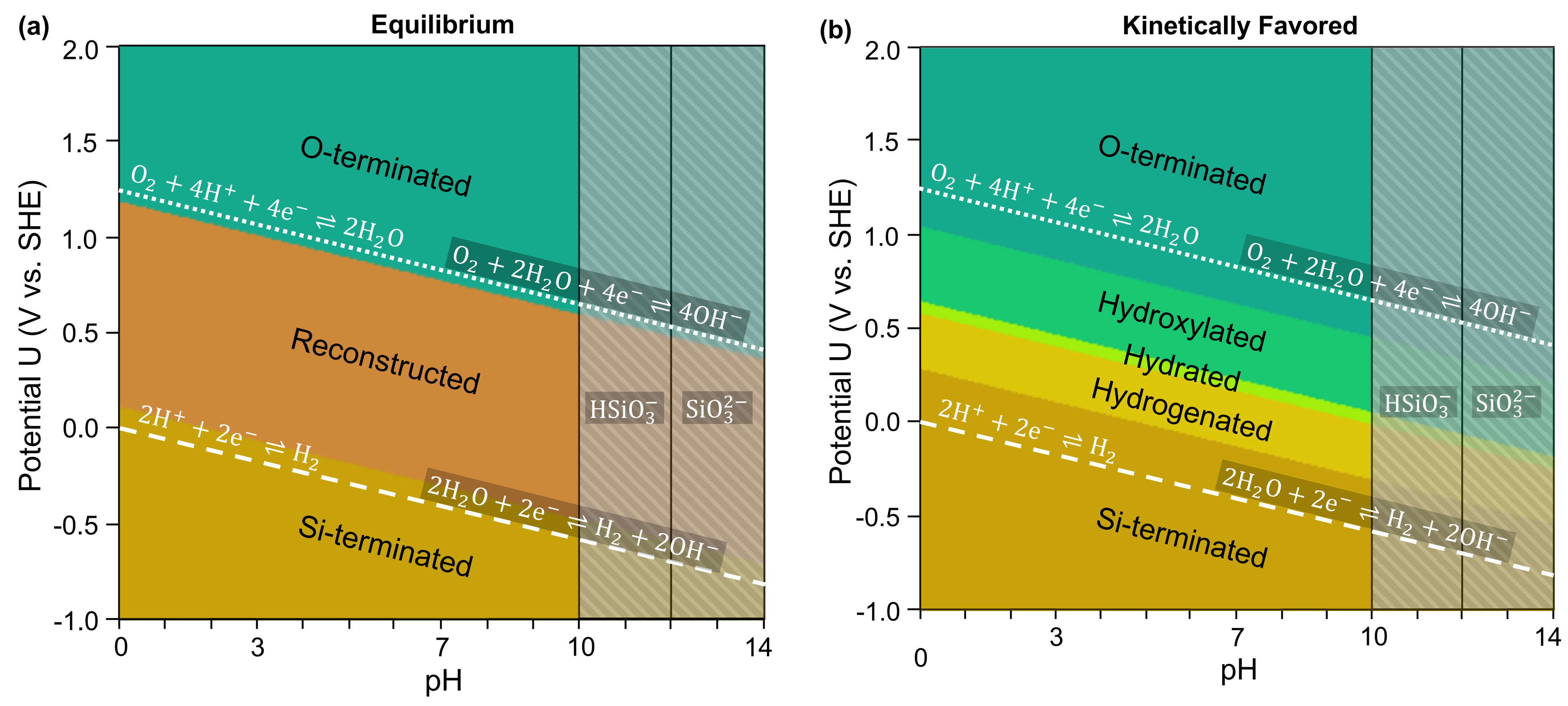
Results

- Previous experimental work has established that the silica membrane is permeable for water, protons, and hydrogen gas.
- Therefore, the buried interface can be expected to respond dynamically to the pH value of the electrolyte.



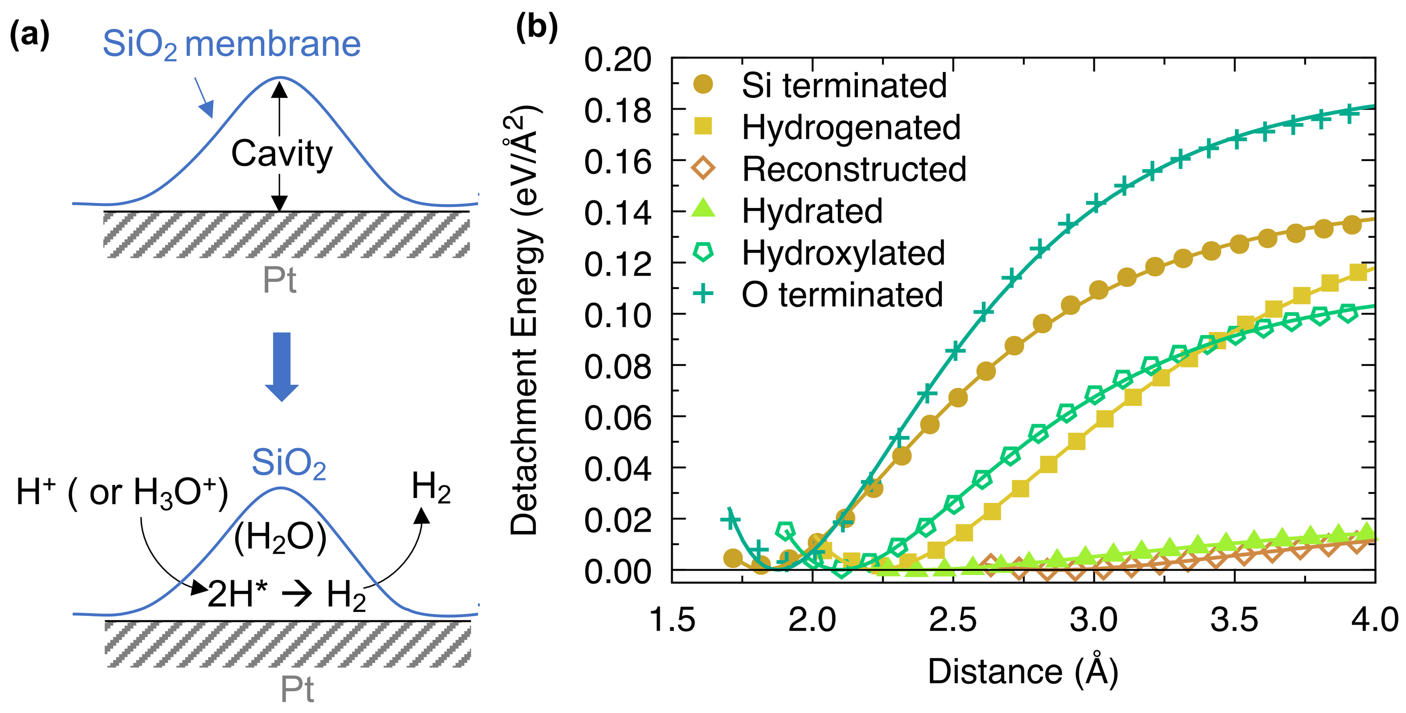
Interface Pourbaix Diagrams

- The interface Pourbaix diagram maps the thermodynamically stable phases.
- The formation of the silica surface reconstruction might be kinetically hindered



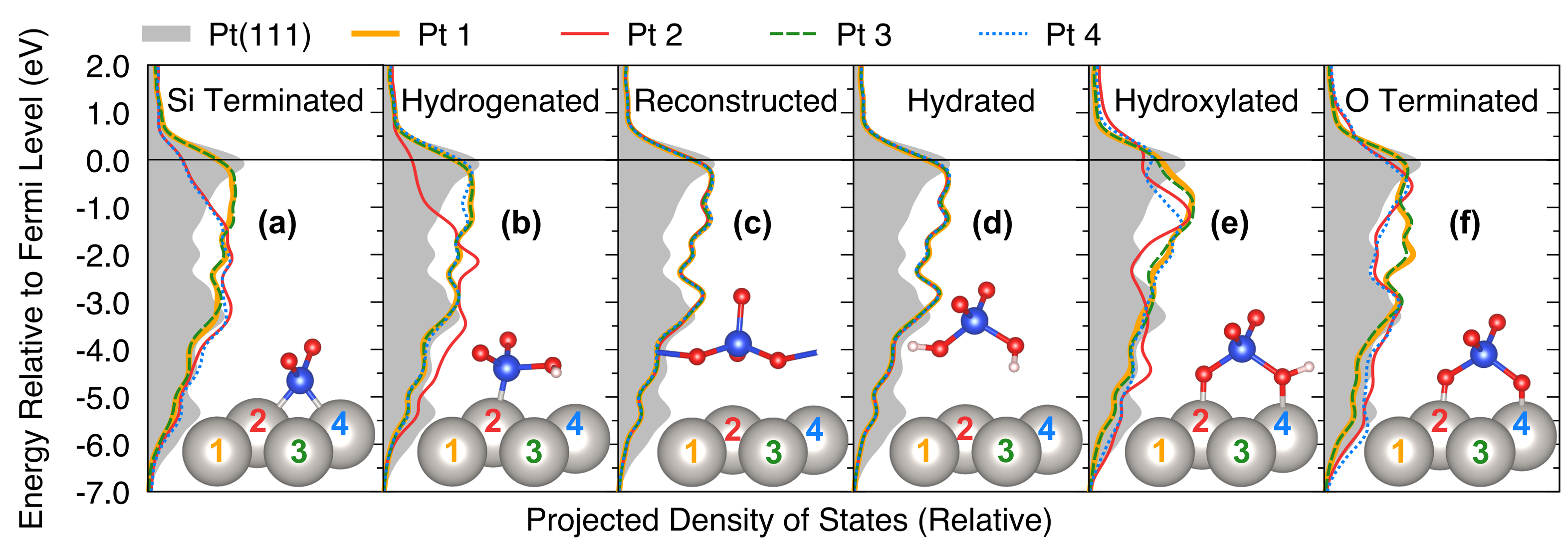
Membrane Adhesion and Detachment

- The pH/potential dependent interactions at the buried interface affect the strength and flexibility of the membrane attachment
- Cavities/voids at the interface might be needed for catalytic reactions to occur.



Electronic Structure of the Catalyst Surface

- The electronic structure of the catalyst surface is also pH/potential dependent.



Summary

- Semipermeable oxide coatings are a promising way for protecting catalysts in corrosive environments, e.g., for seawater electrolysis.
- We developed an interface Pourbaix diagram formalism to map the stable compositions at the interface as a function of the pH value and the electrode potential.
- We showed for SiO_2/Pt that the composition, adhesion energy, and electronic structure of the buried catalyst/membrane interface depend sensitively on pH and potential.
- The silica membrane does not only protect the Pt surface but also changes its properties, showing potential for a synergistic effect of membrane and metal catalyst.

Acknowledgements

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