UNDERSTANDING SILICA COATINGS ON PLATINUM CATALYSTS VIA FIRST-PRINCIPLES POURBAIX DIAGRAMS

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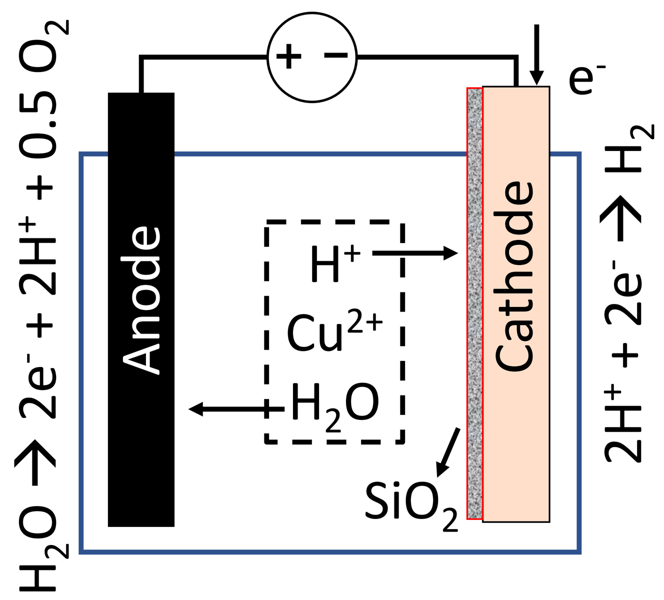
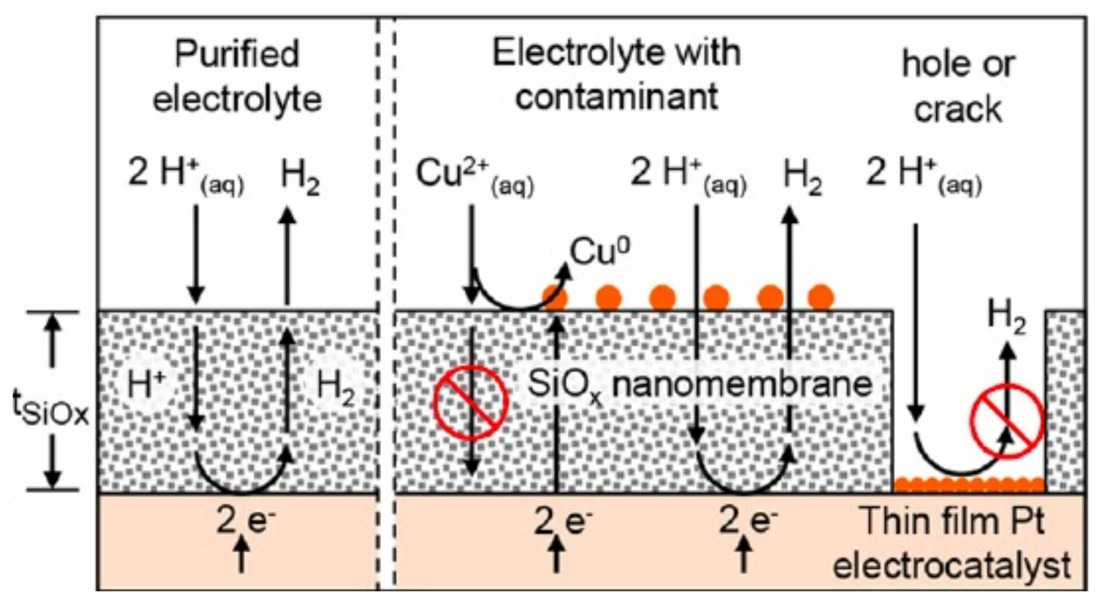
1. Background



- Low-grade water electrolysis with SiO_2 coatings on the cathode as protection layer.

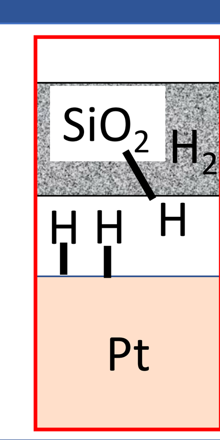


N. Y. Labrador, D. V. Esposito, et al., *ACS Catal.* **2018**, *8* (3), 1767–1778

- SiO_2 coatings (4~15 nm controllable thickness) are semipermeable[1]:
  - ✓ for H^+ and H_2
  - ✗ for contaminants (e.g., Cu^{2+})

2. Research Questions

- What is the structure of the buried SiO_2/catalyst interface?
- How does the interface depend on pH and electrode potentials?
- How does SiO_2 coating affect the reaction mechanisms (e.g., Hydrogen Evolution Reaction (HER))?



3. Methods

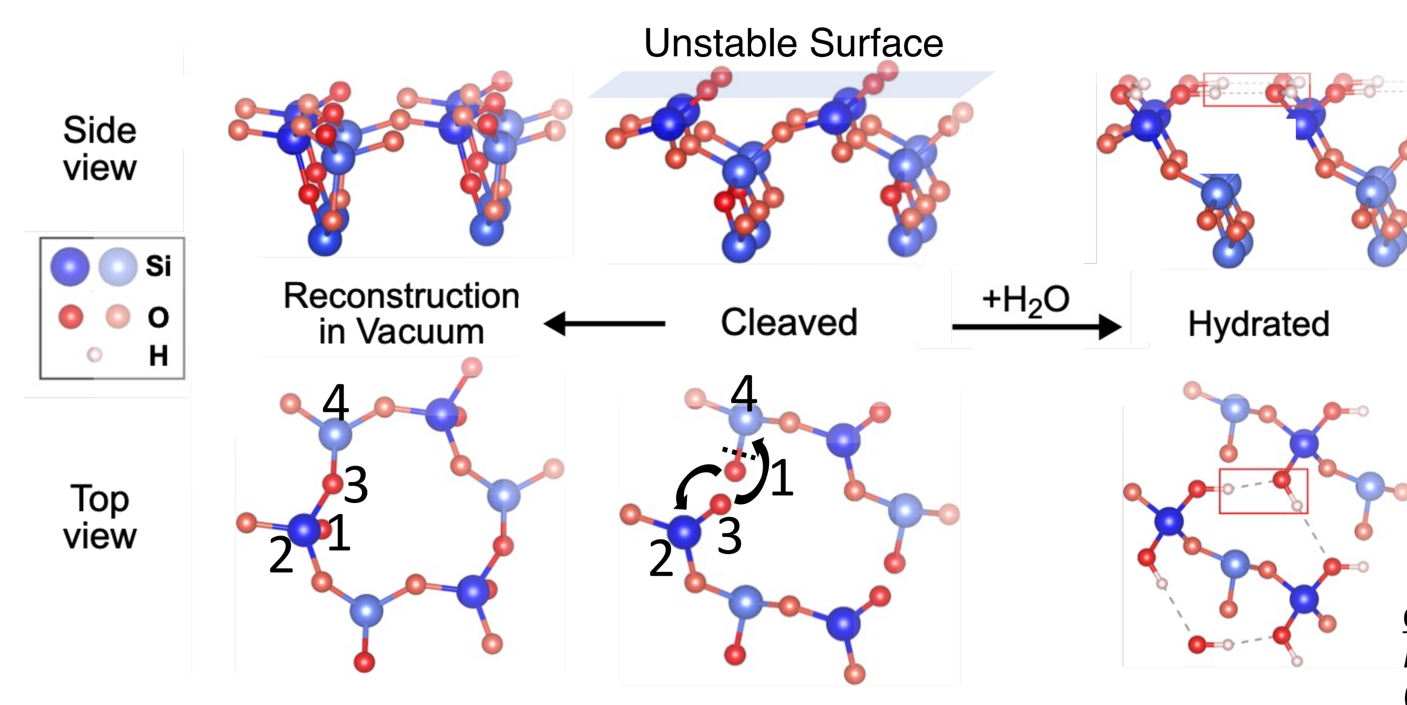
- DFT with the PBE functional and D3 dispersion correction (PBE-D3)
- PAW as implemented in VASP; plane-wave energy cutoff of 520 eV.
- Gamma-centered 3×3×1 k-point meshes
- Nudged Elastic Band (NEB) and machine learning accelerated NEB (ML-NEB)[2]
- Approximate pH- and potential-dependent Gibbs free energy of formation:

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

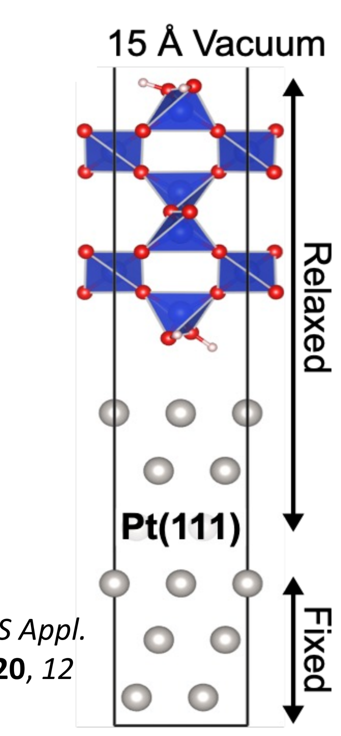
$$\Delta G(\mathrm{pH}, U) \approx E_{(\mathrm{Si_6H_xO_y})/\mathrm{Pt}} - E_{\mathrm{Pt(111)}} - E_{\mathrm{Si_6H_2O_{13}}} - (y-13)E_{\mathrm{H_2O}} - (x-2y+24)\left[\frac{1}{2}\left(E_{\mathrm{H_2}} - TS^{\circ}_{\mathrm{H_2}}\right) - 2.3k_BT * \mathrm{pH} - e * U_{\mathrm{SHE}}\right]$$

4. Results[3]

- Surface reconstruction of crystalline SiO_2:

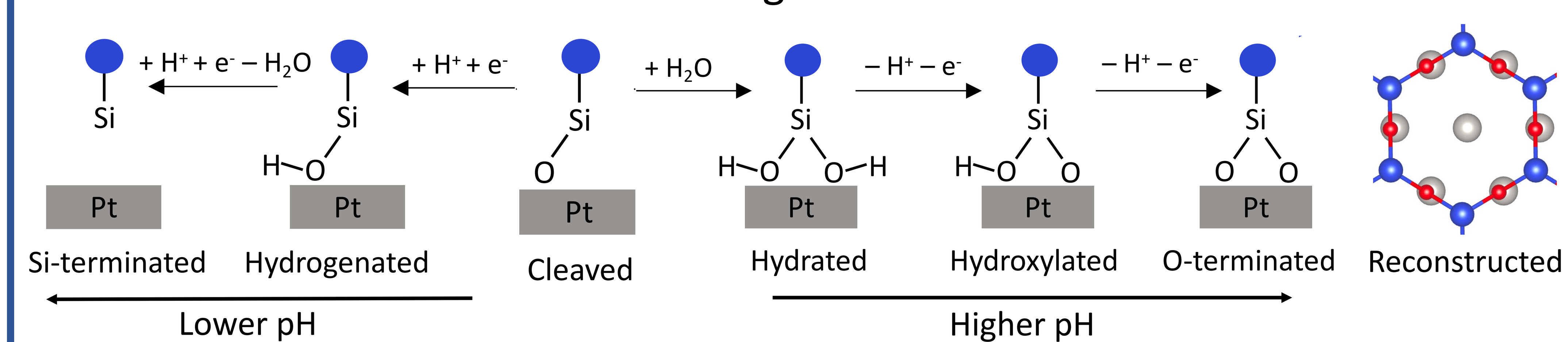


- Interface Model

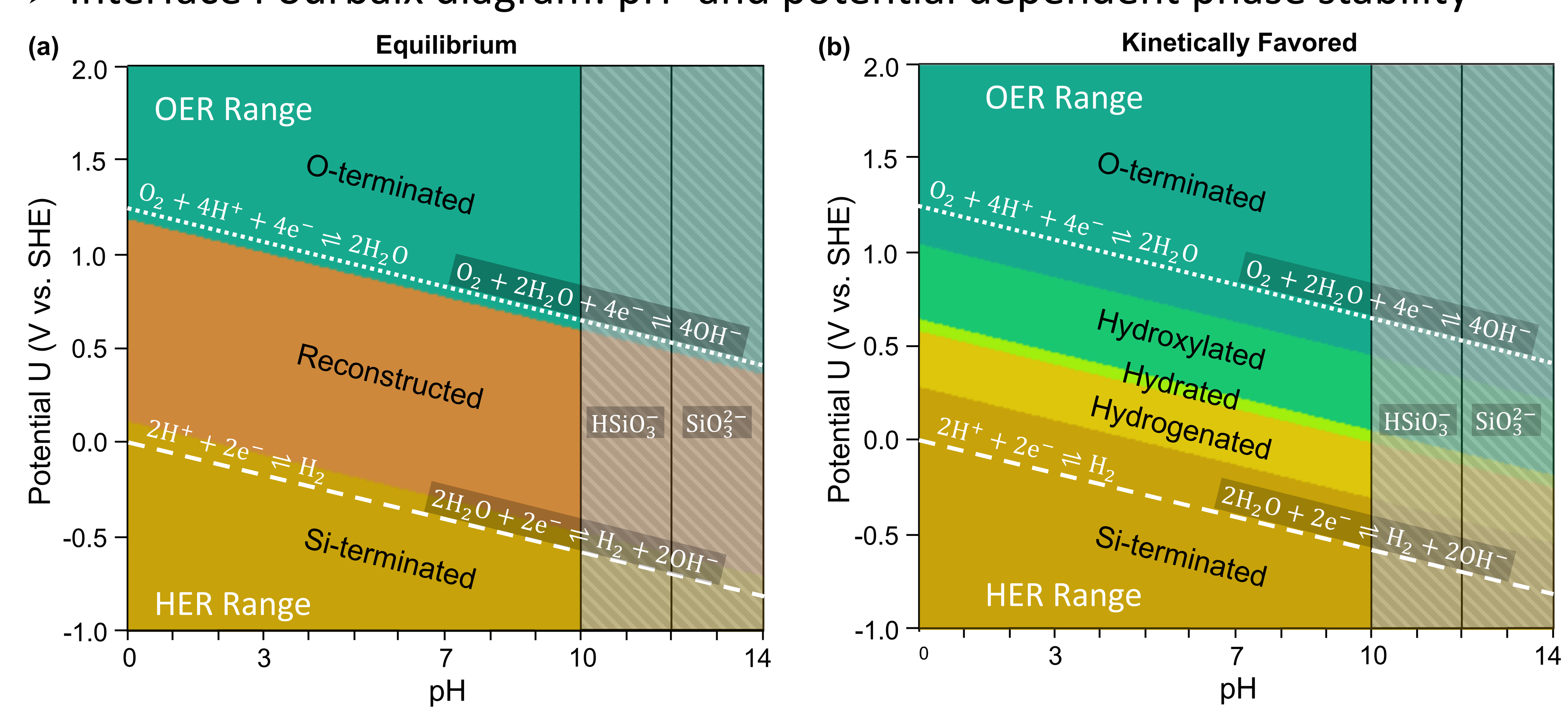


Qu, J., Urban, A., *ACS Appl. Mater. Interfaces* **2020**, *12* (46), 52125–52135.

- A schematic view of interface configurations



- Interface Pourbaix diagram: pH- and potential dependent phase stability



5. Conclusions

- 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 function of the pH and potential
- We showed for SiO_2/Pt that the composition of the buried membrane-coated electro-catalysts (MCECs) interface depend sensitively on pH and potential

References

1. Labrador, N. Y.; Songcuan, E. L.; De Silva, C.; Chen, H.; Kurdziel, S. J.; Ramachandran, R. K.; Detavernier, C.; Esposito, D. V. *ACS Catal.* **2018**, *8* (3), 1767–1778.
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3. Qu, J.; Urban, A. *ACS Appl. Mater. Interfaces* **2020**, *12* (46), 52125–52135.

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