

Supplementary Information for: Micro-Kinetic Model of Electrochemical Carbon Dioxide Reduction over Platinum in Non-Aqueous Solvents

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1 Details of Implicit Solvation Model for Potential Dependence of CO₂ Adsorption

To determine the potential dependence of CO₂ adsorption, grand-canonical constant potential calculations were performed. The Vienna Ab-Initio Simulation Package¹⁻³ was used, with the electrolyte modeled by the polarizable continuum model as implemented in VASPsol.^{4,5} The counter-charge was modeled with the linearized Poisson-Boltzmann equation with a Debye screening length of 3 Å, corresponding to 1.0M electrolyte. Further details of the polarizable continuum can be found in its documentation.^{4,5} To counteract the substantial dipole moment of adsorbed CO₂ (which adopts a bent configuration), charge and countercharge is introduced to obtain constant potential energetics. The potential dependence of CO₂ adsorption depends proportionally to the strength of this dipole moment, which is largely independent of the metal it binds to and rather depends on the configuration of the CO₂ molecule. On Pt (111), this potential dependence was calculated to be 0.2 eV of stabilization per Volt of potential, with CO₂ being stabilized by more reducing potentials.

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2 Coverage Heatmaps

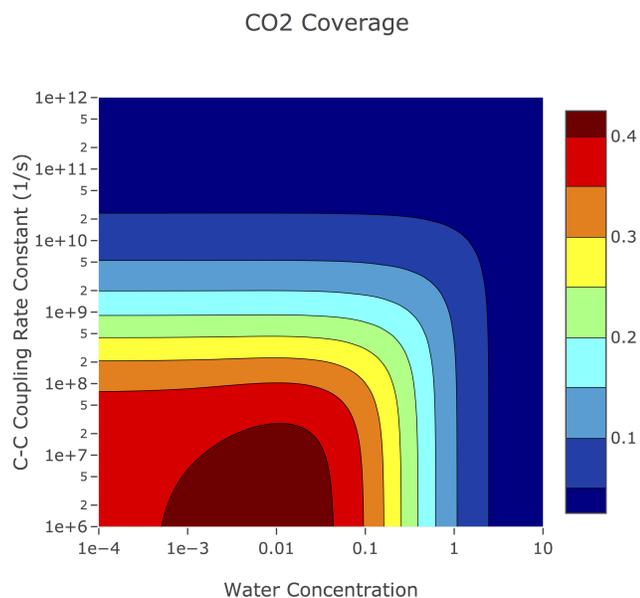


Fig. 1 Model I's estimate of the coverage of surface-bound carbon dioxide as a function of water concentration and the C-C coupling rate constant.

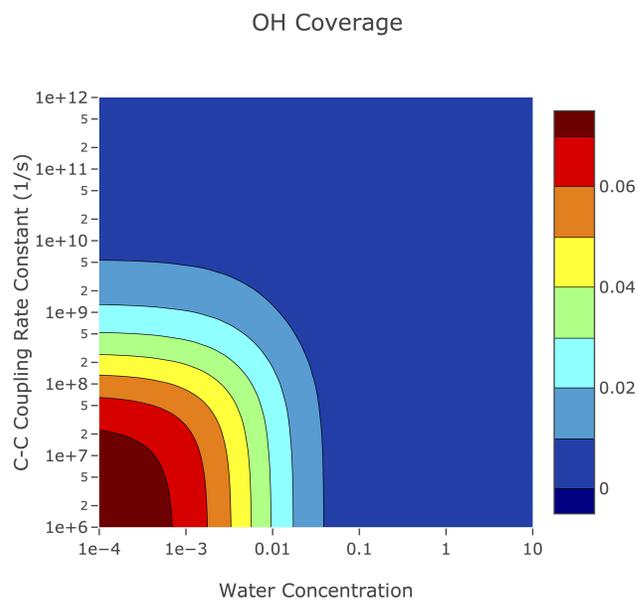


Fig. 3 Model I's estimate of the coverage of surface-bound OH as a function of water concentration and the C-C coupling rate constant.

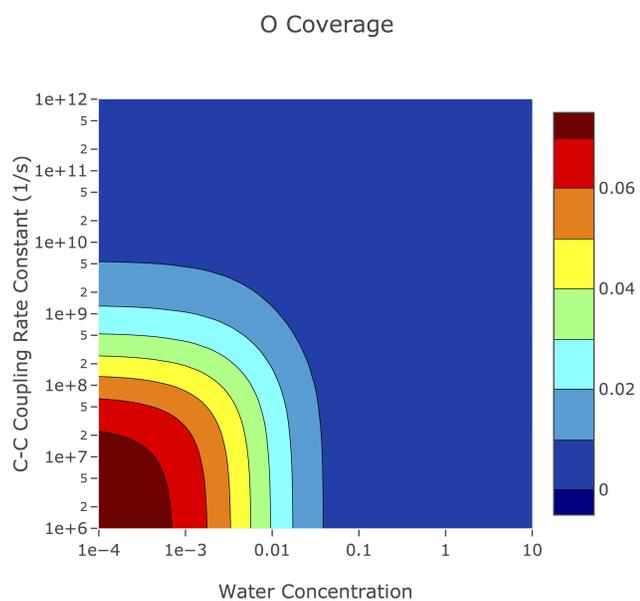


Fig. 2 Model I's estimate of the coverage of surface-bound oxygen as a function of water concentration and the C-C coupling rate constant.

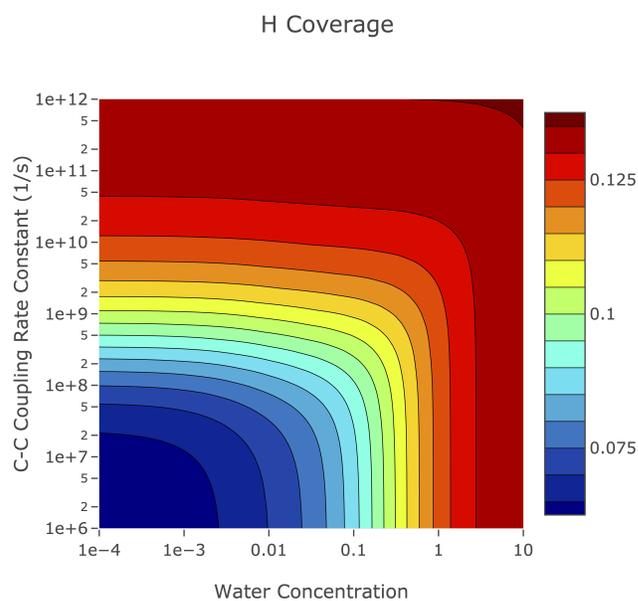


Fig. 4 Model I's estimate of the coverage of surface-bound hydrogen as a function of water concentration and the C-C coupling rate constant.

Empty Site Coverage

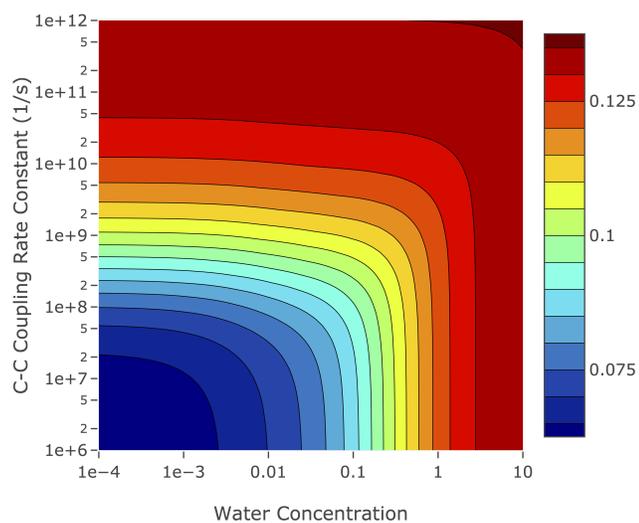


Fig. 5 Model I's estimate of the coverage of empty sites as a function of water concentration and the C-C coupling rate constant.

Notes and references

- 1 G. Kresse and J. Furthmüller, *Physical Review B*, 1996, **54**, 11169–11186.
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- 4 K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. Arias and R. G. Hennig, *The Journal of Chemical Physics*, 2014, **140**, 084106.
- 5 K. Mathew and R. G. Hennig, *arXiv preprint arXiv:1601.03346*, 2016.