Chair of Theoretical Chemistry
TUM Department of Chemistry
Technical University of Munich

Ab Initio Thermodynamics Insight into the Surface Structure of Transition Metal Carbides in Aqueous Electrolyte

Haobo Li* and Karsten Reuter

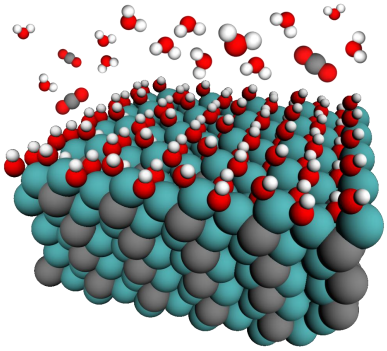
Chair of Theoretical Chemistry, TUM Department of Chemistry, Technical University of Munich, Germany

*E-mail: haobo.li@tum.de

Abstract

A drastic reduction of CO_2 is urgently needed to fight climate change and enable a sustainable growth. The electrochemical reduction of CO_2 (CO2RR) is a promising approach to generate chemical energy carriers from renewable electricity[1]. Transition metal carbides (TMCs) are a promising non-noble material class, with e.g. Mo_2C recently reported to convert CO_2 into CH_4 at low potentials of ~0.55 V[2]. Understanding the surface structure and composition of TMCs under working conditions in the aqueous electrolyte is a prerequisite for ensuing CO2RR mechanistic studies. We therefore conduct *ab initio* thermodynamic calculations to investigate the atomic structure of Mo_2C/aqueous interfaces as a function of potential and pH. The phase transition conditions from the oxidized state to the reduced state at the surface are precisely predicted from a theoretical perspective.

TMCs in aqueous electrolyte



Electrolyte with H_2O and CO_2

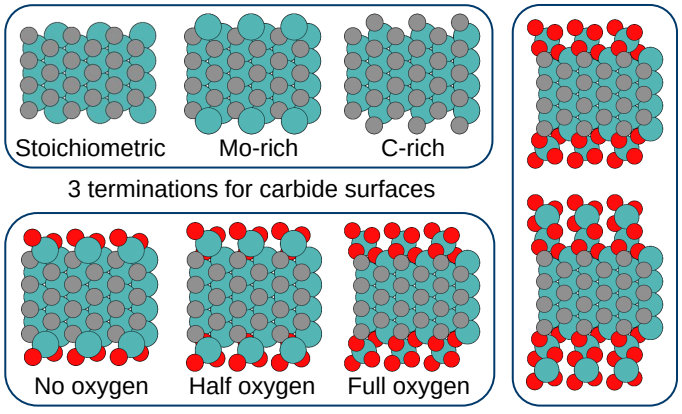
O* or *OH adsorbates

Oxide layer(s)

Metal- or C-terminated surface

TMCs bulk

MoO_2 overlayer(s) on Mo_2C



3 terminations for carbide surfaces

3 orientations at oxide/carbide interfaces 1 or 2 oxide layer(s)

5 surface coverages for *O and/or *OH (0ML, 1/4ML, ..., 1ML)

315 structures for each Mo carbide phase

Ab Initio Thermodynamics Approach

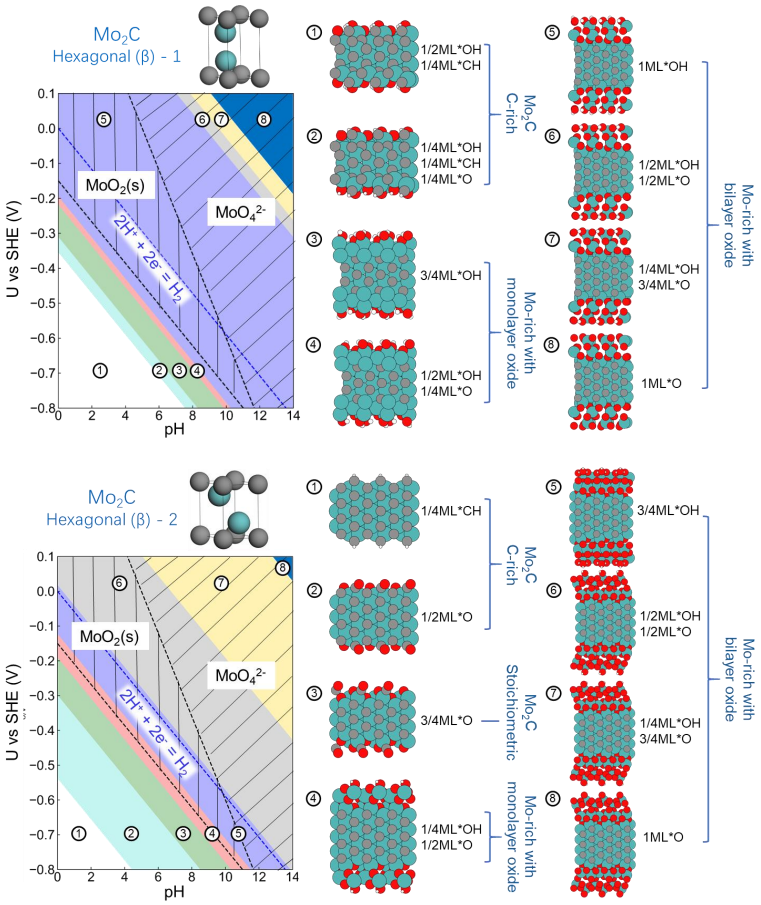
Gibbs free energies: Density functional theory (DFT)

Quantum Espresso + Environ[3]

$$\gamma(U,pH) = \frac{1}{2A}\left[G_{\mathrm{surf}}(\mathrm{Mo}_x\mathrm{O}_y\mathrm{C}_z\mathrm{H}_w) - \frac{x}{2}G_{\mathrm{bulk}}(\mathrm{Mo_2C}) - \left(z-\frac{x}{2}\right)\mu_{\mathrm{CO_2}} - (y-2z+x)\mu_{\mathrm{H_2O}} - (w-2y+4z-2x)\mu_{\mathrm{H}}\right]$$

$$\mu_{\mathrm{H}} = \frac{1}{2}E_{\mathrm{H_2(molecule)}} + F^{\mathrm{vib}}_{\mathrm{H_2}} + eU_{\mathrm{SHE}} - k_B T log_{10}(pH).$$

Surface Pourbaix Diagram



Conclusion

1. With decreasing bias and decreasing pH, the surface changes from an oxidized state to a reduced state.
2. The reduction conditions of the oxide overlayer can be precisely predicted to correspond with the experiments.

References

[1] Y. Hori, *In Handbook of Fuel Cells; John Wiley & Sons, Ltd: Chichester, UK*, **2010**.

[2] S. K. Kim, Y. J. Zhang, H. Bergstrom, R. and A. Peterson, *ACS Catal.* **2016**, 6, 2003.

[3] O. Andreussi, N. G. Hormann, et al. *J. Chem. Theory. Comput.* **2019**, 15, 1996-2009.