Investigation of Au(100) and Au(110) Surfaces by electrochemical Reflection Anisotropy Spectroscopy in HCl and H_2SO_4

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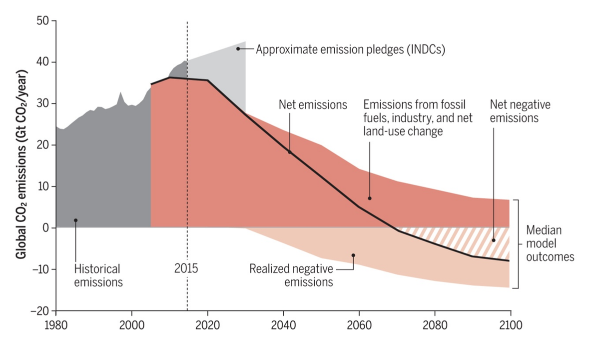
Motivation

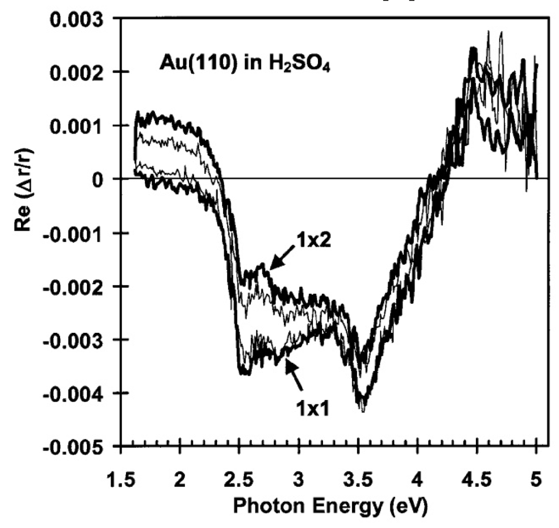
- Due to global warming, active removal of CO_2 from the atmosphere is necessary to reach the target of 2.0 °C warming compared to the pre-industrialised climate.[1]

[2] Anderson et al.



- A potential material that enables the electrochemical reduction of CO_2 to sink products or value-added chemicals is gold.[3]
- We focus on the atomic structure and the interface between gold and electrolyte in different acidic solutions, with and without adding CO_2.
- Investigations by Mazine and Borensztein[6] showed that it is possible to detect the reconstruction of the Au(110) surface with reflection anisotropy spectroscopy.
- Potenital-induced Au(110) surface reconstruction:
  - Below 0.05 V vs Ag/AgCl : (1x2)
  - Above 0.25 V vs Ag/AgCl : (1x1)
- Both reconstructions have distinct RA spectra.
- Gold therefore constitutes an ideal model system to study electrocatalysis involving CO_2.

[6] Mazine et al.



Methods

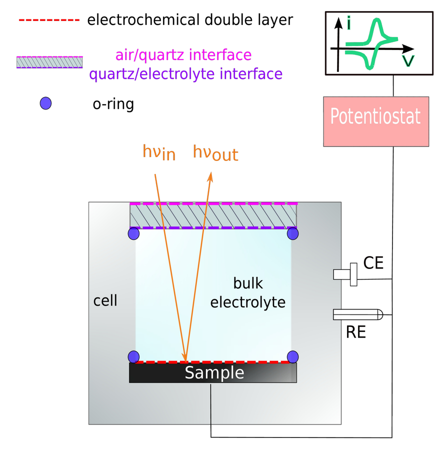
Reflection Anisotropy Spectroscopy (RAS) [4-6]

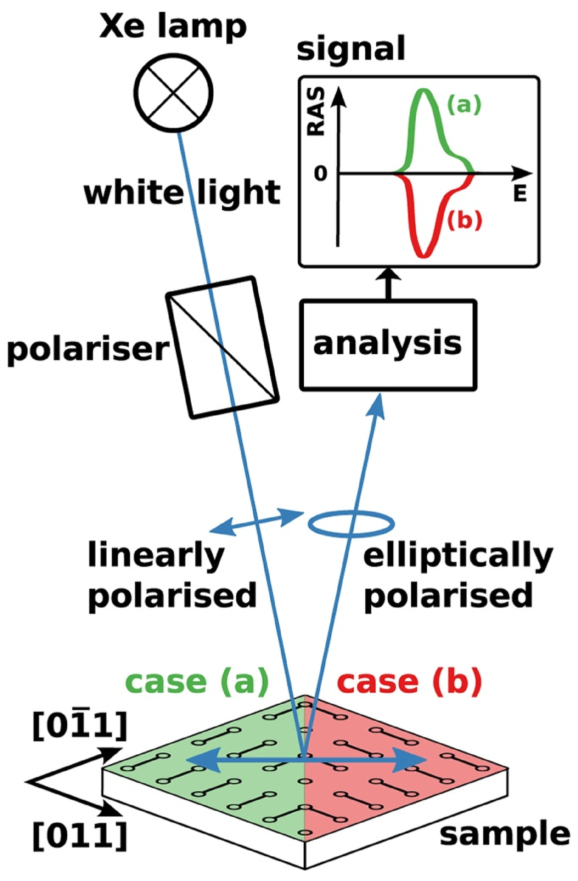
RAS measures the difference in reflectance (Δr) of normal incidence, linearly polarized light between two orthogonal directions in the surface plane (x, y), normalized to the mean reflectance (r).

$$\frac{\Delta r}{r} = 2\frac{r_x - r_y}{r_x + r_y}$$

- High surface sensitivity (monolayers) and time resolution (10 ms).

➔ Operando observation of changes in surface chemistry, surface states, surface reconstruction.

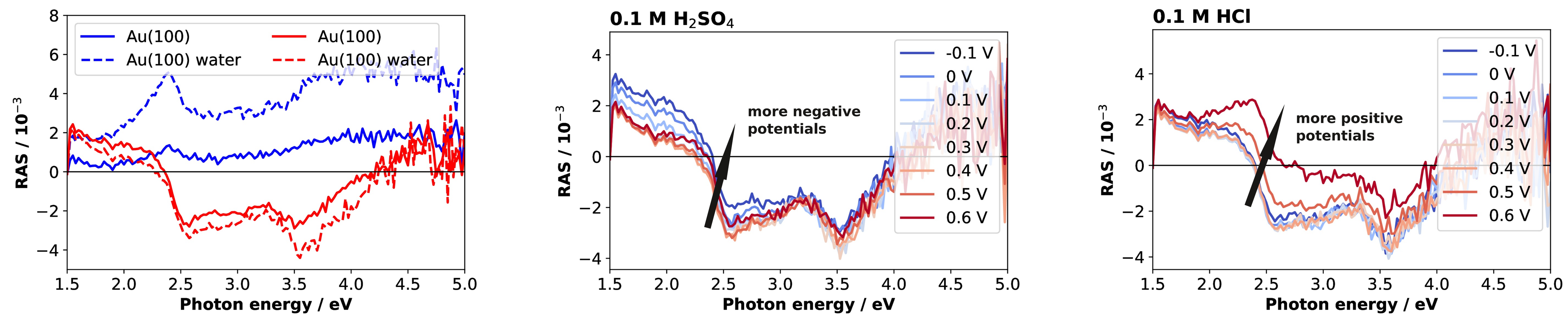




➔ Can be coupled with electrochemical measurements such as Cyclic Voltammetry.

Results

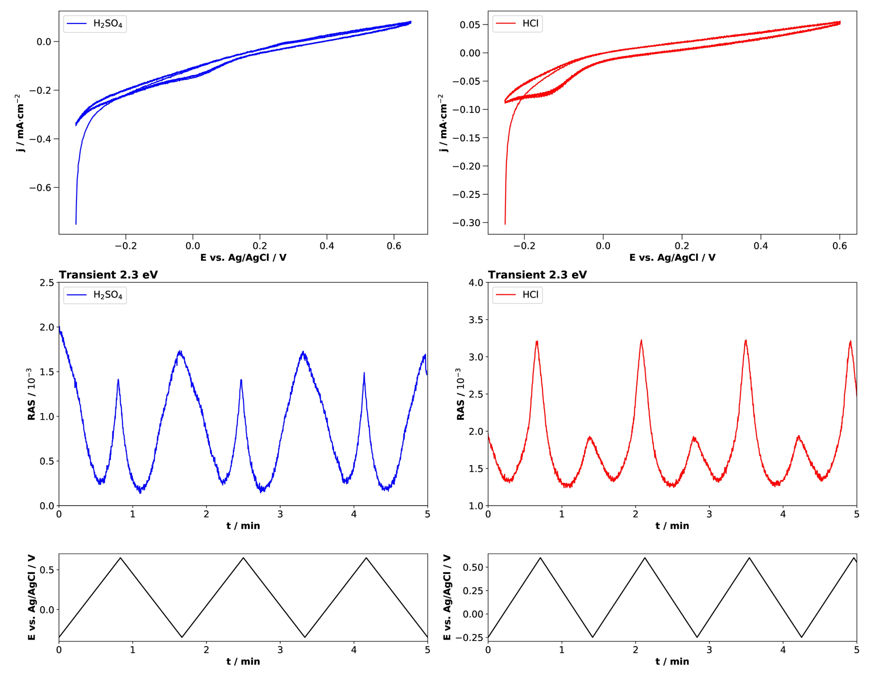
RA-spectra of flame annealed Au(100) and Au(110) in air and water and H_2SO_4 and HCl at different applied potentials



- H_2SO_4
  - below 0.05 V (1x2) reconstruction
  - above 0.25 V (1x1) reconstruction
- HCl
  - -0.15 V - 0.2 V (1x2) reconstruction
  - 0.05 V - 0.4 V (1x1) reconstuction
  - 0.5 - 0.6 V Chloride adsorption
- The potentials are measured vs Ag/AgCl.

- The change in the RA-spectra with different potentials corresponds to the RA-spectra taken by Mazine et al.[7]
- The spectra show a change in the surface reconstruction of Au(110) from the (1x1) reconstruction at higher potentials to the (1x2) reconstruction at lower potentials.
- The peak at 2.3 eV corresponds to chloride adsorption on the gold surface.[8,9]

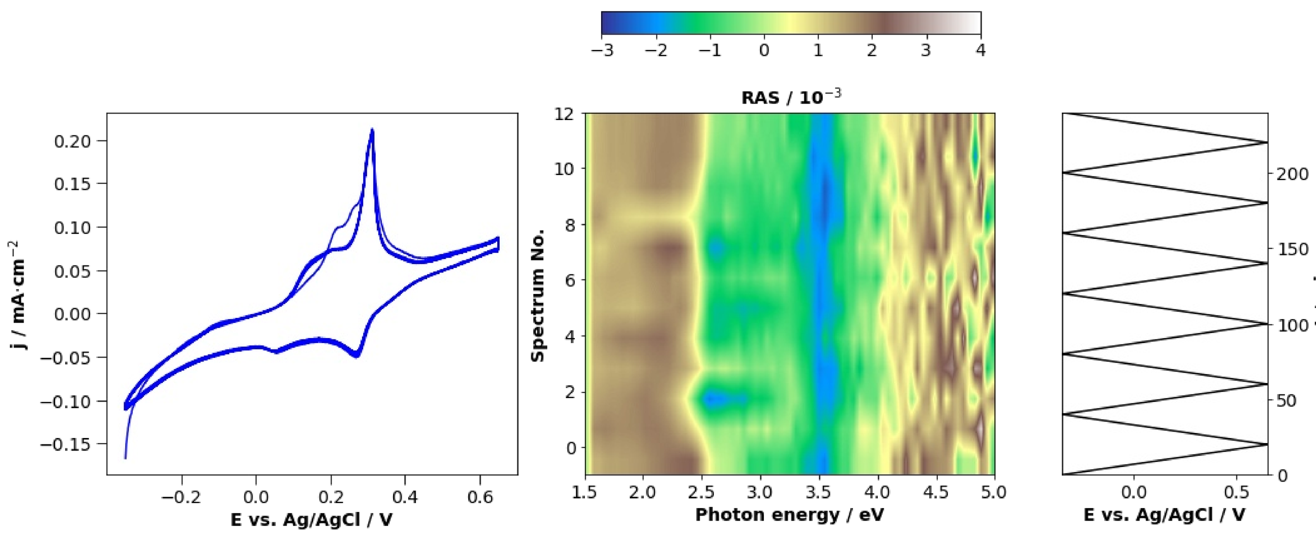
Cycling Au(110) in 0.1 M electrolyte

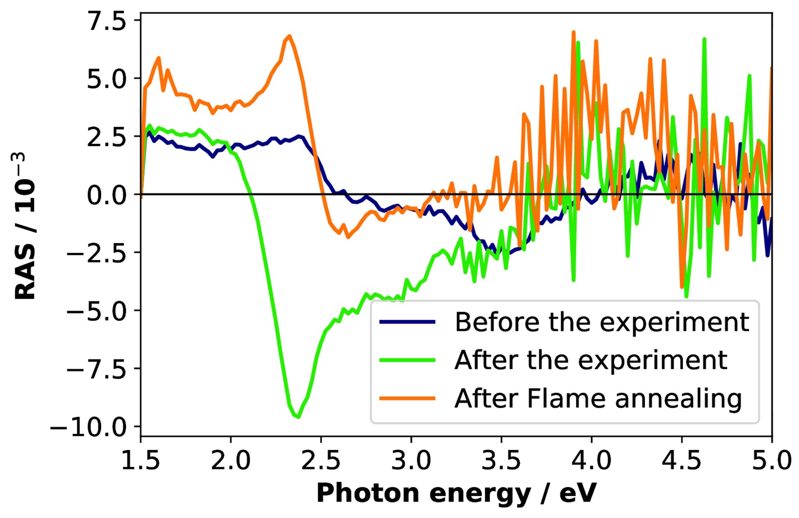


- Reversible peaks correspond to the reconstruction of the Au(110) surface and chloride adsorption on the surface. There might be trace amounts of chloride in H_2SO_4.[10]

Cycling Au(110) in 0.1 M HCl and CO_2

- 0.1 M HCl saturated with CO_2
- CV: -0.35 V to 0.65 V 0.05 V/s 6 Cycles





- We observe an irreversible change of the interface structure upon the insertion of CO_2 into the electrolyte. This might indicate catalyst poisoning, for instance by CO.
- Change in the colour plot are also impacted by surface roughening.

- During the experiment, the surface changed drastically due to surface roughening.
- EDX shows carbon contamination on the surface.
- It was not possible to regain the original surface by flame annealing.

Summary

- We can observe the reconstruction of the Au(110) surface as a reversible process during cycling in different electrolytes by RAS.
- The shoulder that appears at high potentials at 2.3 eV belongs to the adsorption of the chloride on the surface.
- Adding CO_2 to the electrolyte leads to oxidation and reduction during cycling.

➔ This appears to introduce an irreversible change of the interfacial ordering, which requires further investigations.

Outlook

- Investigate the reaction with CO_2 in more detail to improve understanding.
- Transfer experiment to H_2SO_4 to probe dependence on electrolyte composition.
- Do the same experiments with Au(100) to investigate structure-sensitivity.
- Computational RAS for more detailed understanding (ongoing).

References

[1] May, Matthias M., and Kira Rehfeld. Earth System Dynamics 10.1 (2019): 1-7.
[2] Anderson, Kevin, and Glen Peters. Science 354.6309 (2016): 182-183.
[3] Marcandalli, Giulia, Matias Villalba, and Marc TM Koper. Langmuir 37.18 (2021): 5707-5716.
[4] Weightman, P., Martin, D. S., Cole, R. J., & Farrell, T. (2005). Reports on Progress in Physics, 68(6), 1251.
[5] Goletti, C. Encyclopedia of Interfacial Chemistry, Elsevier, Oxford, (2018), 413–420.
[6] May, M. M., Lewerenz, H. J., & Hannappel, T. (2014). The Journal of Physical Chemistry C, 118(33), 19032-19041.
[7] Mazine, V., and Y. Borensztein. Physical Review Letters 88.14 (2002): 147403.
[8] Kolics, Artúr, Aliston E. Thomas, and Andrzej Wieckowski. Journal of the Chemical Society, Faraday Transactions 92.20 (1996): 3727-3736.
[9] de Moraes, Ines R., and Francisco C. Nart. Journal of Electroanalytical Chemistry 461.1-2 (1999): 110-120.
[10] Magnussen, O. M., J. Wiechers, and R. J. Behm. Surface Science 289.1-2 (1993): 139-151.

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