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Supporting Information

The Effect of Anions and pH on the Activity and Selectivity of an Annealed Polycrystalline Au Film Electrode in the Oxygen Reduction Reaction-Revisited

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The Effect of Anions and pH on the Activity and Selectivity of an Annealed Polycrystalline Au Film Electrode in the Oxygen Reduction Reaction - Revisited

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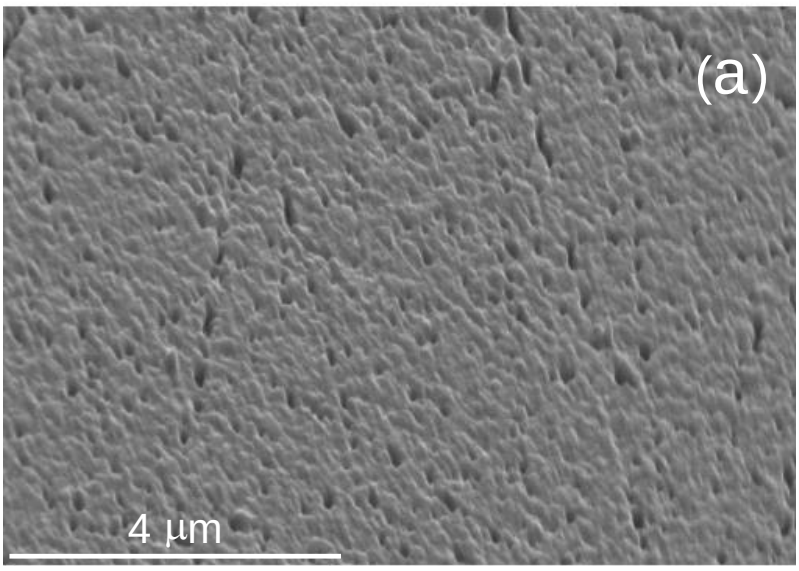
Morphology of the Au Film Electrode

Secondary Electron Microscopy (SEM) characterization of an annealed Au film electrode shows homogeneously distributed nanocrystallites (Fig. S1a). Statistical evaluation yields an average grain size of around 200 nm (Fig. S1b). It should be noted, that the Au particle grain size can affect the spectral features of interfacial water.[1;2]

As an additional surface structure sensitive probe, we employed the underpotential deposition of lead (Pb-upd), which had been employed earlier for the electrochemical characterization of the surface structure of annealed gold films.[3-6] The sharp spikes for Pb-upd at ca. 0.0 V (Fig. S1c) are comparable with the equally sharp Pb-upd peaks observed for stepped Au single crystal electrodes showing (311), (221), (322) and (544) orientations as examples for the (111)-(110) zone, and (755), (533) and (211) orientations as examples for the (100)-(111) zone.[5] Overall, the voltammetric profiles do not allow an unambiguous structural assignment. In particular, they are not characteristic for (100) oriental facets as dominant structural element.



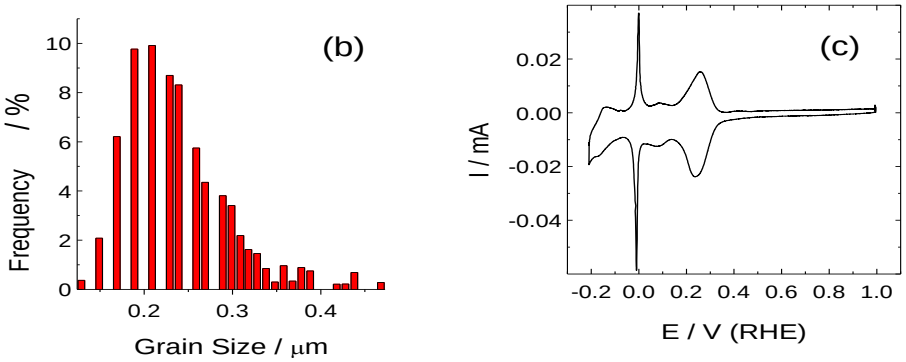


Figure S1 (a) SEM image of the morphology of an annealed Au film electrolessly deposited on a Si prism (magnification 50000); (b) statistical distribution of the grain size; (c) Pb-upd in 1.0 M $HClO_4$ solution containing 1.0 mM of Pb^{2+}, potential scan rate 10 mV s^{-1}, electrolyte flow rate ca. 40 μl s^{-1}.

Potential-dependent ATR-FTIR Spectra

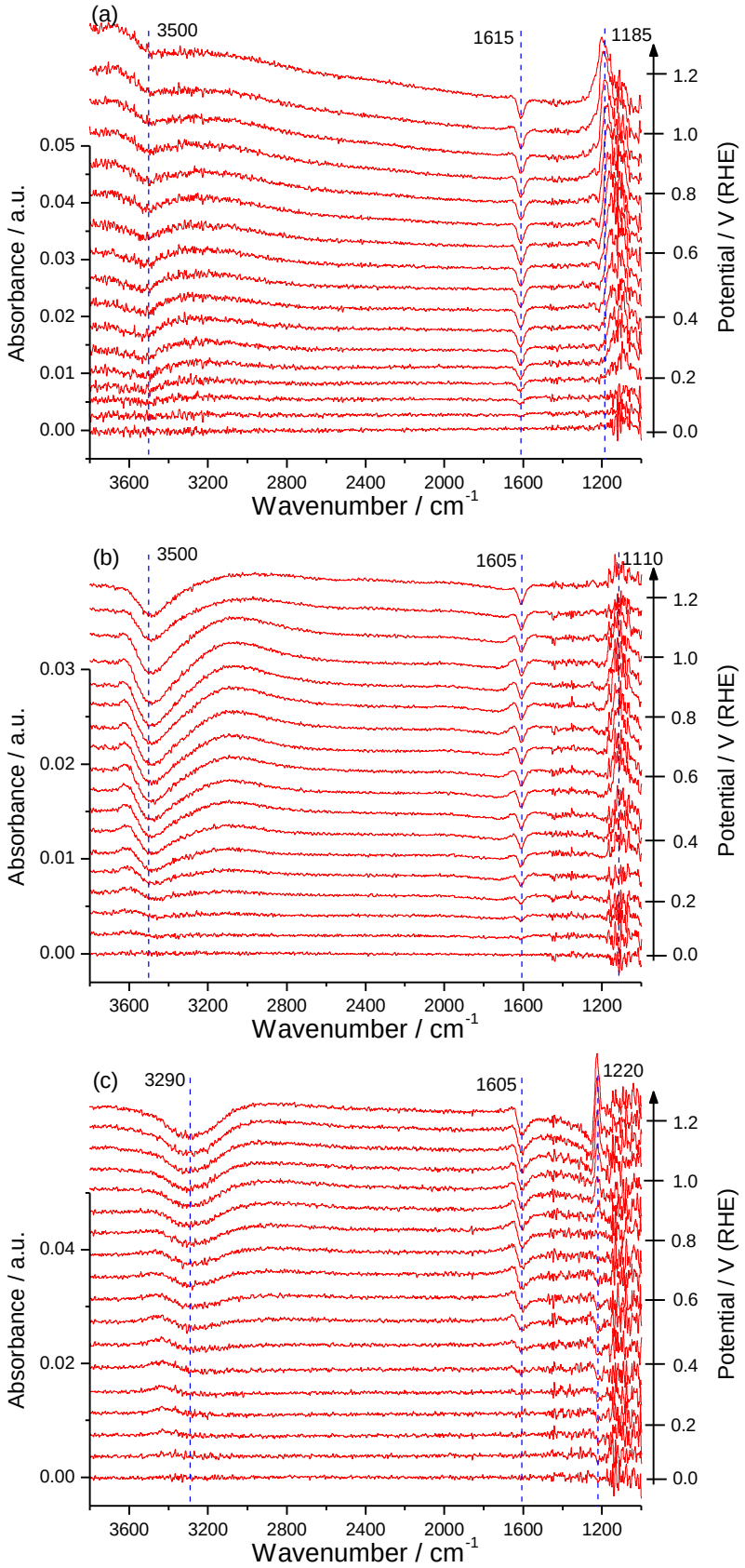


Figure S2 Selected potential-dependent ATR-FTIR spectra recorded during a positive-going potentiodynamic scan in different O_2-free electrolytes from 0.0 V to 1.2 V (potential scan rate 10 mV s^{-1}, electrolyte flow rate ca. 40 µl s^{-1}), similar as in Figures 4a, 5a, 6a, but using background spectra at 0.0 V in O_2-free supporting electrolyte as reference (spectral resolution 4 cm^{-1}, time resolution 1 s^{-1}, for clarity each 10^{th} spectrum is shown). a) 0.5 M sulfuric acid solution, b) 1.0 M perchloric acid solution, c) 1.0 M sodium hydroxide solution.

Potentiostatic ORR Current Transients

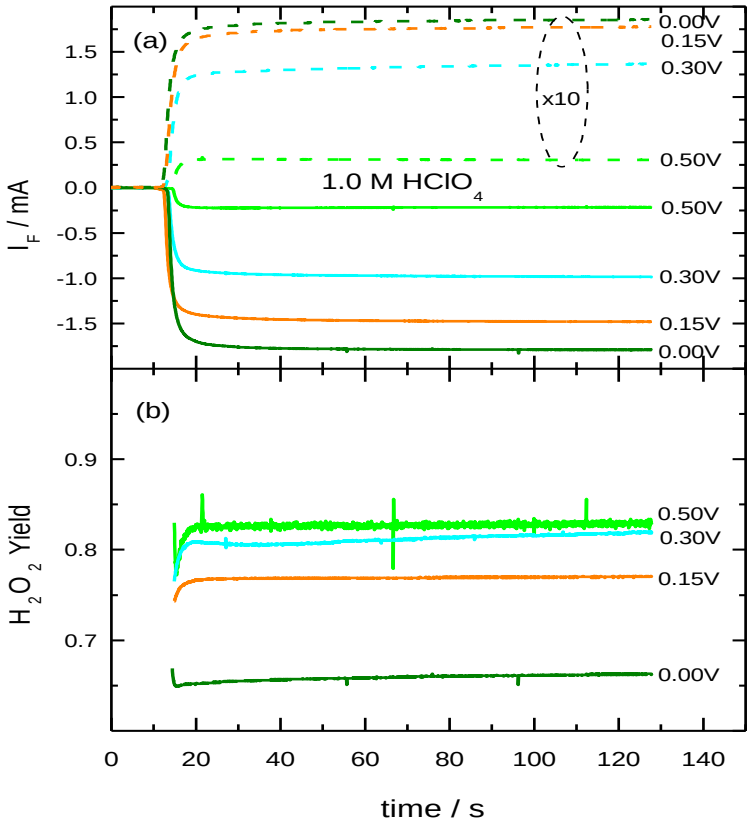


Figure S3 Potentiostatic current transients of a) the ORR and the HPOR and b) the resulting relative H_2O_2 yield in O_2-saturated perchloric acid base electrolyte on the annealed Au film electrode at different potentials (1.0 M $HClO_4$, electrolyte flow rate ca. 40 µl s^{-1}). The current transients were recorded upon switching from the O_2-free supporting electrolyte to O_2-saturated electrolyte at constant potential.

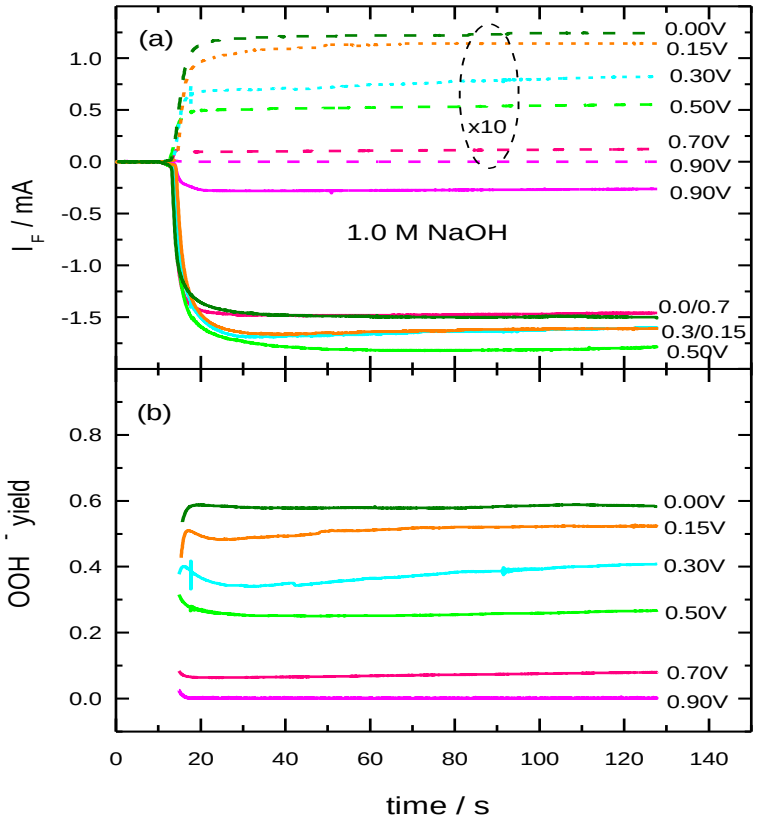


Figure S4 Potentiostatic current transients of a) the ORR and the HPOR and b) the resulting relative H_2O_2 yield in O_2-saturated alkaline base electrolyte on the annealed Au film electrode at different potentials (1.0 M NaOH, electrolyte flow rate ca. 40 µl s^{-1}). The current transients were recorded upon switching from the O_2-free supporting electrolyte to O_2-saturated electrolyte at constant potential.

Reference List

[1] N. Garcia-Araez, P. Rodriguez, V. Navarro, H.J. Bakker, M.T.M. Koper, *J. Phys. Chem. C* **2011**, *115*, 21249-21257.

[2] N. Garcia-Araez, P. Rodriguez, H.J. Bakker, M.T.M. Koper, *J. Phys. Chem. C* **2012**, *116*, 4786-4792.

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[4] A. Hamelin, A. Katayama, *J. Electroanal. Chem. Interfac. Electrochem.* **1981**, *117*, 221-232.

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[6] J. Hernandez, J. Solla-Gullón, E. Herrero, *J. Electroanal. Chem.* **2004**, *574*, 185-196.