Anodic Oxidation of Gold Electrodes in 0.1M Perchloric Acid Investigated using EXAFS

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Introduction and Setup We have studied the oxidation of polycrystalline gold electrodes in 0.1 M perchloric acid at moderate current densities ($\leq$ 0.5 mA/scm). This investigation is an extension of a study of this oxidation process at high current densities ($\geq$ 50 mA/scm $\leq$ J $\leq$ 650 mA/scm) [1]. Electrodes were oxidised in 0.1M perchloric acid and subsequently emersed under potential control into an XAFS cell continuously flushed with helium. Details of this setup are reported elsewhere [2]. All spectra were taken under He gas-flow in total electron-yield (TEY) detection mode using a biased stainless steel ring as the electron collector.

Results and Discussion Data analysis was performed (1) as in our previous report [1], by linear combination of the EXAFS and of the XANES spectra and (2) by a full EXAFS analysis using the most recent version of the UWXAS package [3]. Some results of our studies are shown in fig. 1. By linearly combining Au L_3 edge spectra of Au_2O_3 and Au metal the spectra of all oxidised electrodes could be reproduced. Additionally, an EXAFS analysis using the two shortest single-scattering paths in gold (12 Au atoms) and gold(III) oxide (4 O atoms) was carried out employing two different physical models. Throughout this analysis all datasets were fitted *simultaneously* using the FEFFIT and FEFF8 codes. The edge-shift E_0, the overall amplitude factor S_0^2, the Debye-Waller term σ^2 and the single-scattering path length ΔR were chosen to be *global* variables in the fit. First, the fraction of spectral contributions arising from metallic Au (gold^0) was determined for each *individual* dataset. As expected, this analysis yielded the same results as the linear combination techniques previously applied. The percentage of gold^0 contributions to the EXAFS appeared to depend exponentially on the total charge Q flown through the electrodes.
To test this proposition quantitatively, we included an exponential function $P_{Au} = exp(-\mu \cdot Q)$ in our fitting model. The advantage of this approach is that it lowers the number of variables needed for the fit, thereby affording statistically more robust fits and the determination of error margins for the exponential attenuation factor μ. The results obtained by this simplified technique compared well with those of the individual fits.
Assuming an electron origination depth of about 1000 Å and a detection limit for the chemical composition of the sample of approximately 1%, we can state that down to oxide thicknesses of 10 Å no other oxide than amorphous Au_2O_3 appears to be formed during the oxidation process. This holds true for current densities from 0.1 mA/scm to 650 mA/scm. Applying a potential in the range of premonolayer oxidation never yielded a detectable change in the spectra.

Plotting the percentage of Au^0 signal in the spectra over the total charge flown through the electrode shows that the efficiency of the oxidation process (i.e., the fraction of charge) is nearly constant in the range from 50-650 mA/scm. At lower current densities, the efficiency was enhanced by several orders of magnitude (see fig. 2). The reason is likely to be the presence of turbulent and convective flow of the electrolyte in the immediate vicinity of the electrodes at high current densities. This flow is induced by the electrolytic generation of gas bubbles as well as by heat production. It favours the dissolution of oxidised gold over the formation of an oxide layer at the electrode. The EXAFS analysis also indicated that the structural properties of the oxide layers were identical at all current densities investigated in our studies.

Figure 1: Full EXAFS Analysis of selected spectra at 0.5 mA/scm

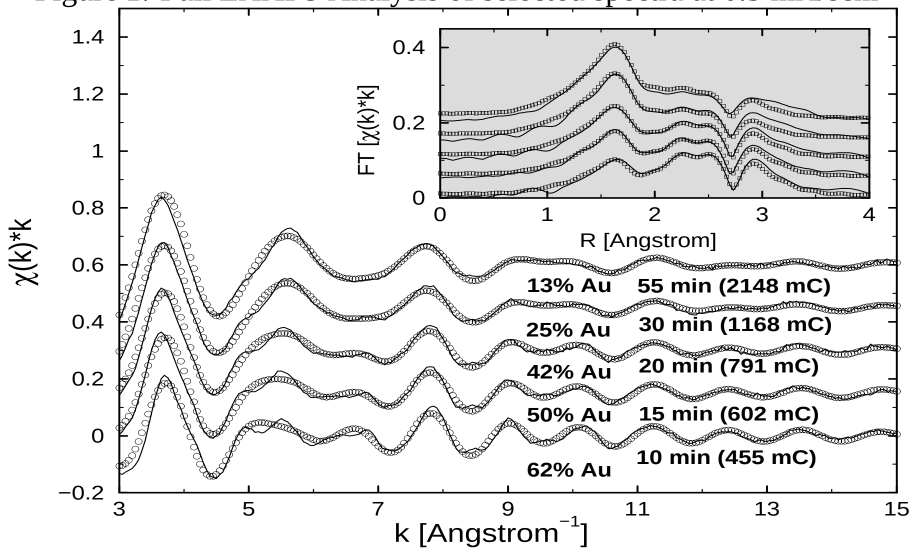
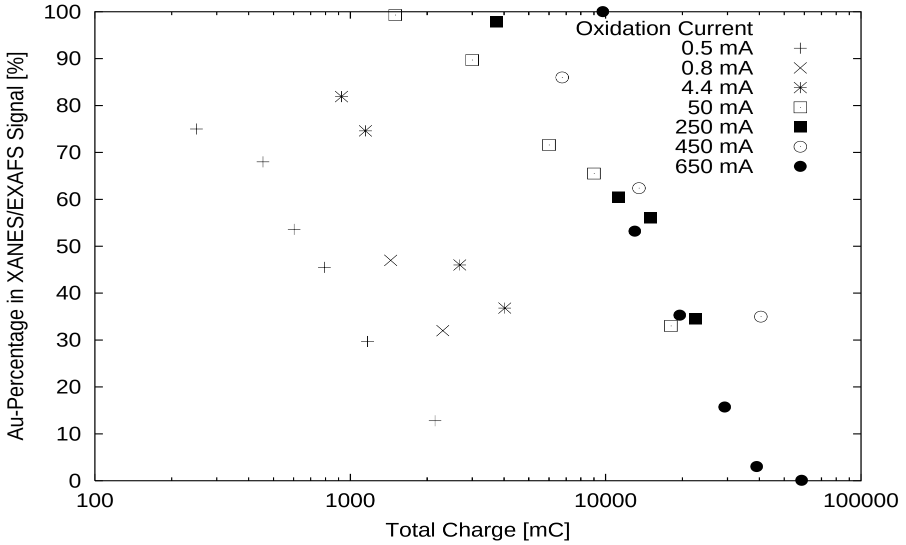


Figure 2: Au^0 Signal as a Function of Total Charge



References

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