Making a Au-Hg Electrode

General principle: Reduction of Hg^{2+} salt in an acidic aqueous solution to deposit a Hg film on a Au electrode. Most divalent Hg salt could be used in conjugation with an acid with the same counter anion, e.g. $HgCl_2$ + HCl.

Experimental details:
Polish a commercial Au electrode according to the procedures outlined in the BAS manual. Prepare an aqueous solution with 1 M HCl serving as both the electrolyte and the proton source. Record a CV of this "blank" solution from 0.5 V to -1 V using Au as the working electrode, Pt wire as the counter electrode, and SCE as the reference electrode. This CV shows a reduction wave at ca. 300 mV vs. SCE, indicating that Au has a low overpotential for H_2 evolution in water. Dilute the solution for 10 times and record the CV again. The reduction wave shift ca. 60 mV in the negative position, as predicted by the Nernst equation.

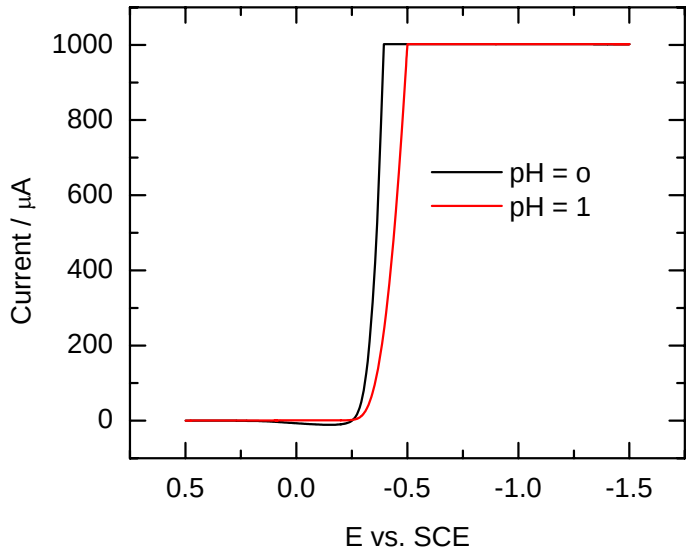

Figure 1. CV of aqueous HCl solution recorded on a Au electrode.

$HgCl_2$ (10 mM) was added to this "blank" solution (pH = 1). After all the Hg salts are dissolved, record a CV from 0.5 V to -1 V. This CV exhibits a reduction peak at ca. -100 mV vs. SCE, corresponding to the Hg^{2+}/Hg couple. The H^+ reduction peak shifts from -400 mV to ca. -1 V on the first scan. An Hg film is already visible after this CV scan. The solution is then electrolyzed at -200 mV for 10 min to deposit a Hg film on the whole surface of the Au electrode. The electrode is then rinsed with MeOH and water, and left to dry in air.

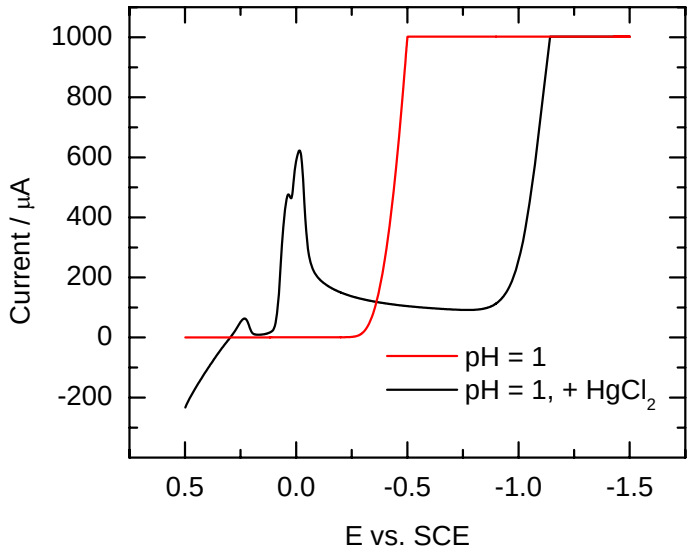

Figure 2. CV of aqueous HCl solution recorded on an Au electrode, in the absence and presence of 10 mM $HgCl_2$.

Record a CV of a pH = 1 aqueous solution using this modified electrode. A sharp peak at ca. -100 mV is found, together with an H^+ reduction wave at ca. -1.2 V. Further electrolysis at -0.15 V does not result in the disappearance of this Hg^{2+}/Hg peak. The Au/Hg electrode is now ready to use.

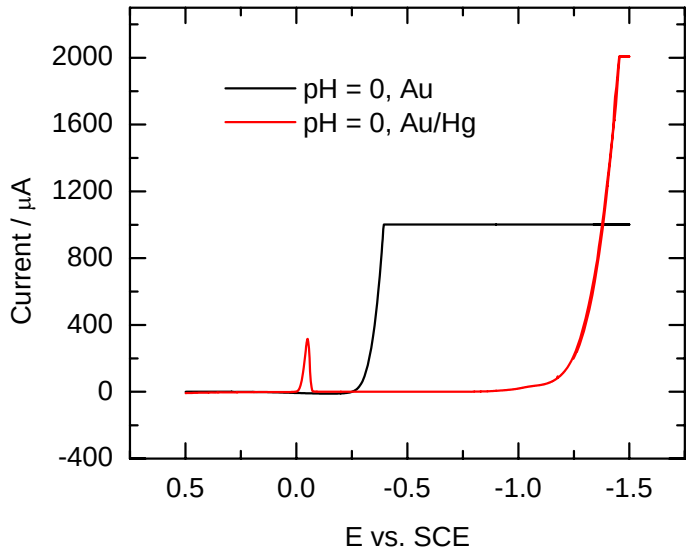

Figure 3. CV of aqueous HCl solution recorded on the Au or Au/Hg electrode.

Identical results are obtained regardless whether argon gas is used to purge the solutions to main an anaerobic environment. A CHI potentiostat was used.