

Electrode Reactions of Iron Oxide-Hydroxide Colloids

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Supplementary Material

Fast accumulation of iron sucrose on a static mercury drop electrode.

For this purpose, a mercury drop was extruded from the capillary into the sample solution and scanned immediately at a rate of 4 Vs^{-1} , thereby completing within 0.4 s (Figure S1).

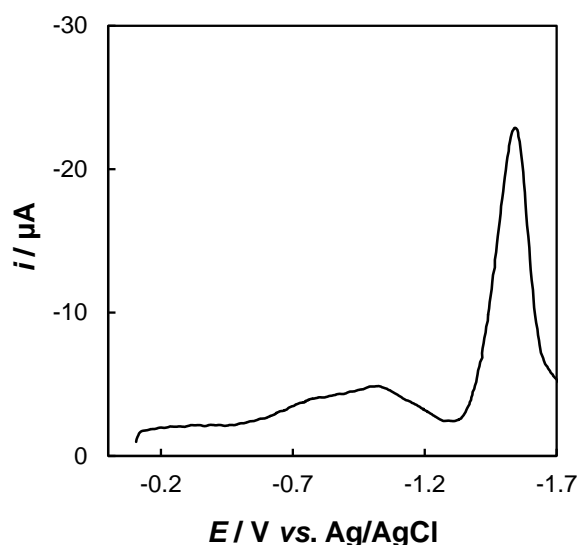


Figure S1. 20 μl iron sucrose added to 10 ml 1.1 M sodium acetate, static Hg electrode, sweep rate 4 Vs^{-1} , total Fe(III) concentration: 1.43 mM.

The ratio between first and second wave integrals is 0.31 here. The sharp wave is shifted to even more negative potential compared to records with slower scan rate, which is typical for an irreversible reaction. The shapes of both waves are characteristic for electrode reactions of adsorbed species. Because the current of the first wave drops to the background level before the second current starts, integrals are well-defined here, and complete consumption of the material causing the first wave is established.

Increased cluster size leads to smaller currents.

The maghemite preparation ferumoxytol, with polyglucose sorbitol carboxymethyl ether as stabilizer, has a larger cluster size than iron sucrose. It produces a similar voltammetric two-wave pattern as iron sucrose and also shows accumulation. However, currents are much weaker at identical total Fe(III) concentration. This reflects the lower diffusion rate of larger clusters and their lower adsorption tendency because of higher mass to contact surface ratio.

Fe(III) citrate condensation at $\text{pH} > 12$.

Voltammograms taken with a static mercury electrode at $\text{pH} = 12$ and $\text{pH} = 13$ are shown in Figure S2. At $\text{pH} = 12$ the electroactive species do not significantly accumulate on the electrode, the current is obtained mainly under diffusion control. The sharpening of the more positive wave at $\text{pH} = 13$ indicates some adsorption, while the second wave appears, like in the polarography experiments of Lingane and Meites [Refs. 13, 14 in the main article].

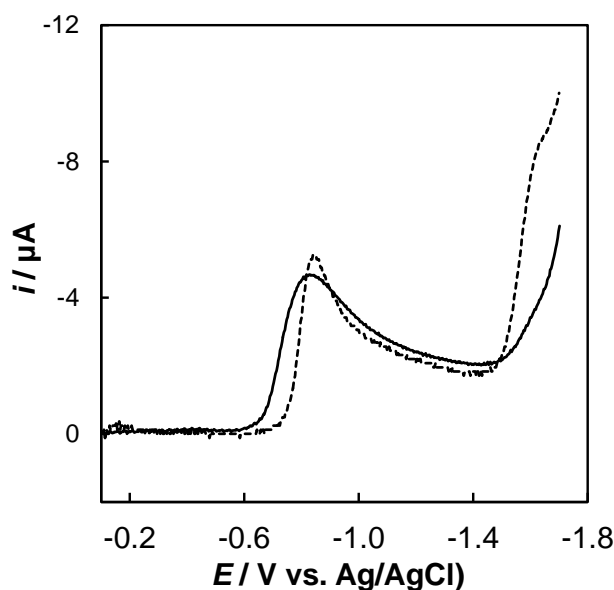


Figure S2. Voltammetric reduction of 2 mM Fe(III) in 0.5 M sodium citrate, solid line: pH = 12, dashed line: pH = 13, static Hg electrode, sweep rate 0.1 Vs^{-1} .

The more negative wave at pH = 13 is too small to account for an $\text{Fe(II)} \rightarrow \text{Fe(0)}$ reduction, and it is produced by a compound that does hardly exist at pH = 12.

Iron sucrose: polarographic limiting currents vs. $t^{1/6}$ (Ilkovic relation)

The limiting currents of the polarograms in Figure 3B do not follow the theoretical relation concerning drop time for a diffusion-controlled reaction ($i_{lim} \propto t^{1/6}$):

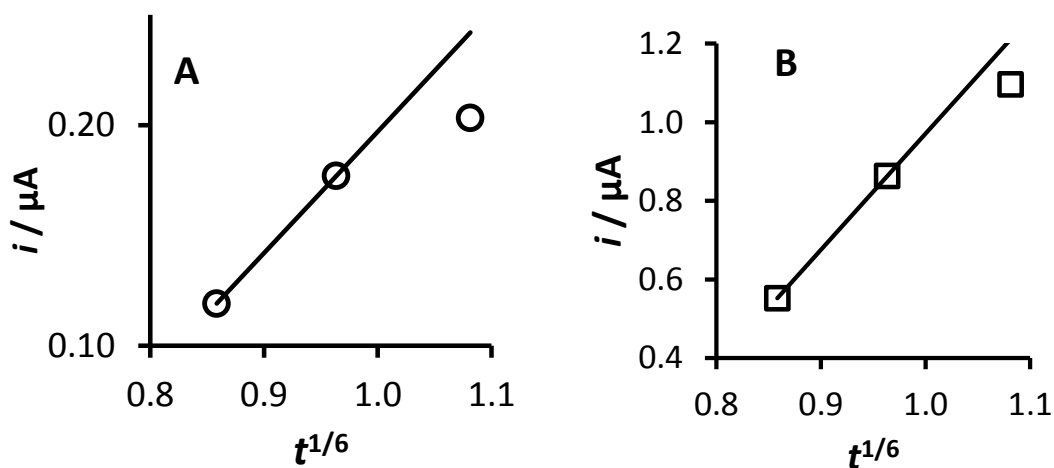


Figure S3. Limiting currents from polarograms in Figure 3B plotted vs. $(t_{\text{drop}})^{1/6}$. A: wave at $-0.6 \text{ V vs. Ag/AgCl}$; B: wave at $-1.4 \text{ V vs. Ag/AgCl}$. Drop times: 0.4, 0.8 and 1.6 s.

Integration approach to estimate transferred charge in the stationary electrode experiments

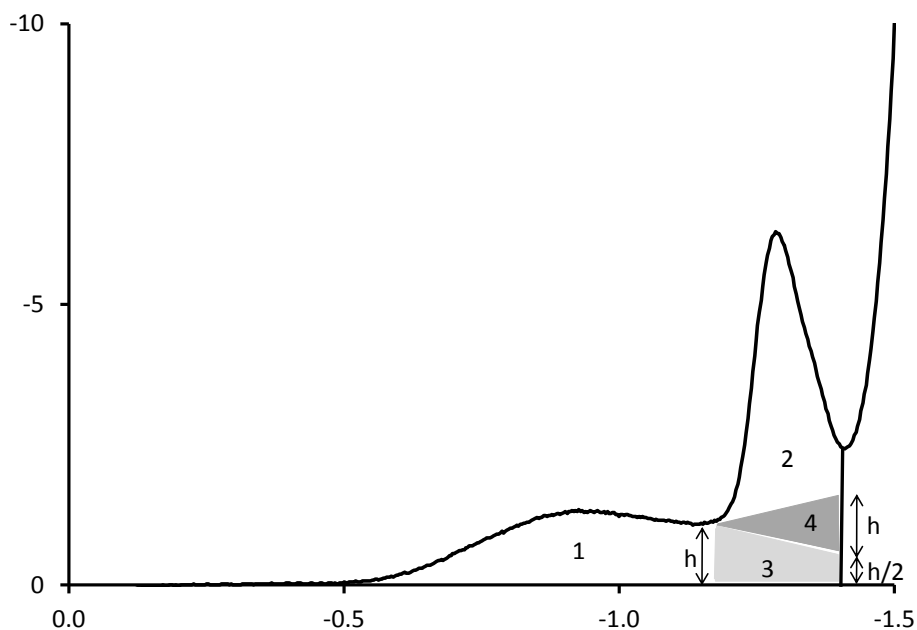


Figure S4. Scheme for the estimation of transferred charge from linear sweep voltammograms obtained with stationary electrodes.

Procedure:

- 1) The baseline recorded with supporting electrolyte only is subtracted from the raw signal. The result is a curve like in Figure S4.
- 2) Numerical integration of areas 1 and 2', which is the sum of 2, 3 and 4
- 3) Calculation of areas 3 and 4
- 4) The area assigned to the first wave is calculated as sum of areas 1 and 3
- 5) The area of the second wave is taken as area 2' minus areas 3 and 4

Area 4 is assumed to be a good approximation to the contribution of the exponentially rising background current.

Survey X-ray photoelectron spectra

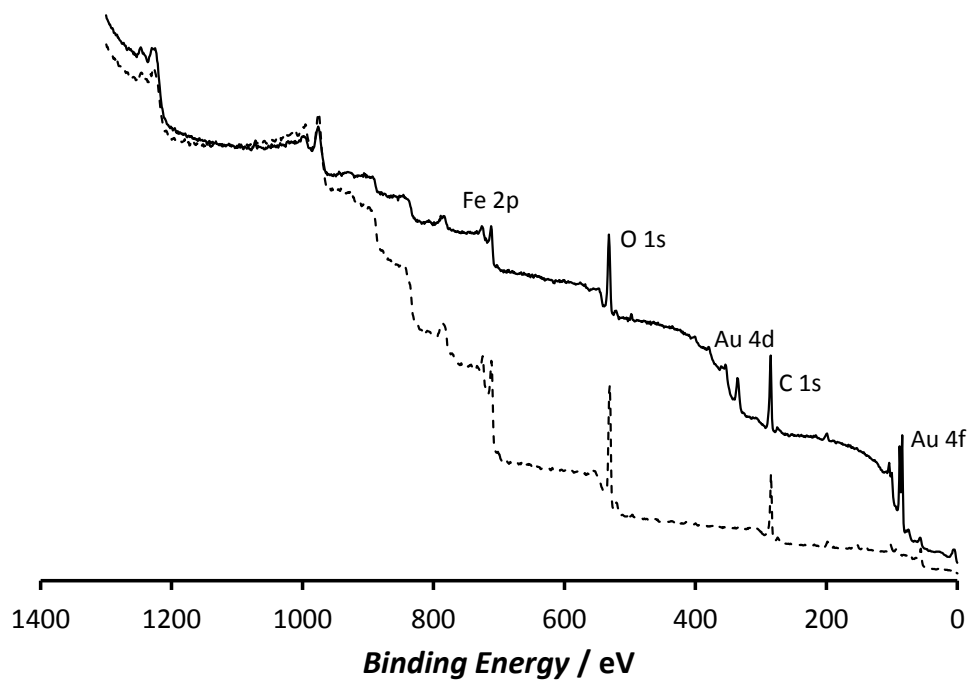


Figure 5S. Survey XPS of iron sucrose on Pt (dashed line) and on Au after partial electrochemical reduction (solid line).