Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Surface enhanced resonance Raman spectroscopy of iron Hangman complexes on electrodes during electrocatalytic oxygen reduction: Advantages and problems of common drycast methods

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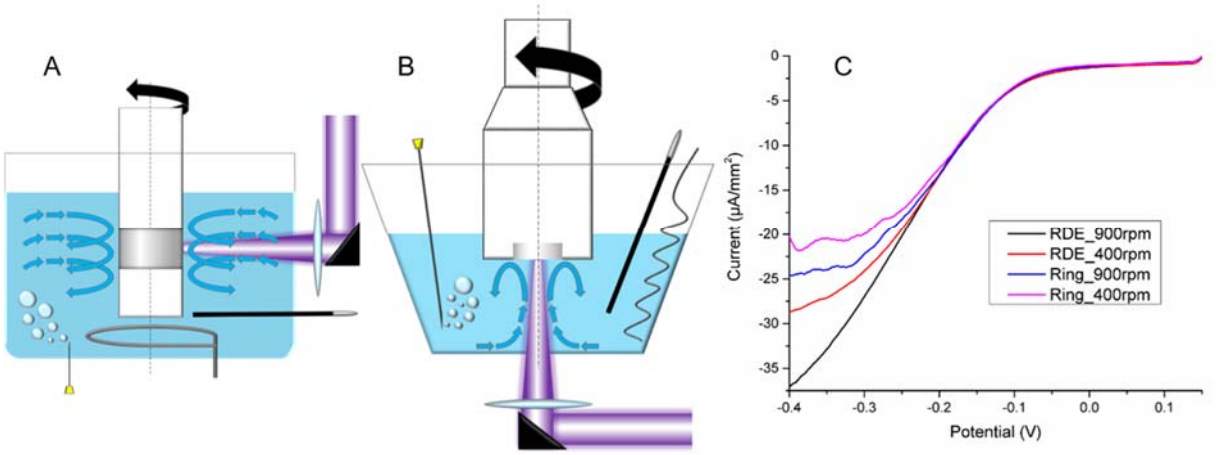

Figure S 1: Ring electrode on the incubation holder (A); RDE setup for Raman measurements (B). ORR of the Ag electrode (C) under oxygen saturated phosphate buffer (100 mM, pH7) conditions for ring and RDE system, LSV with 0.1 V/s, Potential vs. Ag/AgCl 3 M KCL Reference electrode.

The ring and disc electrode setup was tested with respect to their respective capability to promote oxygen reduction of a silver working electrode. Linear sweep voltammetry (LSV) was performed at different rotation rates for both systems. It becomes obvious that the dynamic aspects during the catalytic process are similar for both systems. The onset potential and the diffusion limitation start exactly at the same potential sweep. Furthermore, the linear increase of the current as a function of potential (-0.1 V to -0.2 V) during the LSV is identical for both setups, which implies that the same number of molecules in the solution can react at the same over potential. Therefore, both systems seem to have the same diffusion limitation behaviour. The difference between the maximum current of both systems for the diffusion limitation is determined by the flow characteristics of the buffer solution in the different setups shown in. Due to the physical orientation of both systems, the ring exhibits a weaker suction at the same rotation rate compared to the RDE. Accordingly, the ring electrode reaches the same diffusion limit currents at a higher rotation rate per minute, as exemplarily indicated in with a rotation speed of 900 rpm for Ring and 200 rpm for RDE in Figure S1 B.

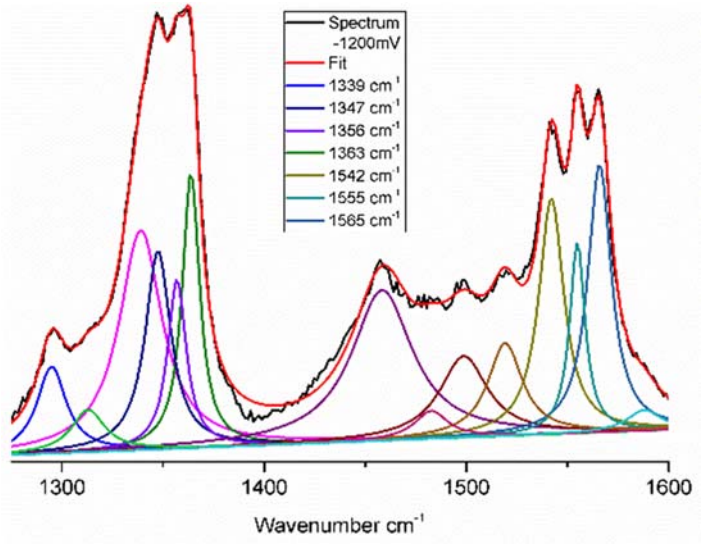

Figure S 2: Fit of the Hangman spectrum (Figure 2 trace a). The measurements were using a home-made software.[21] A band analysis was performed. For this, each spectrum was fitted by the same set of bands to obtain comparable intensities.

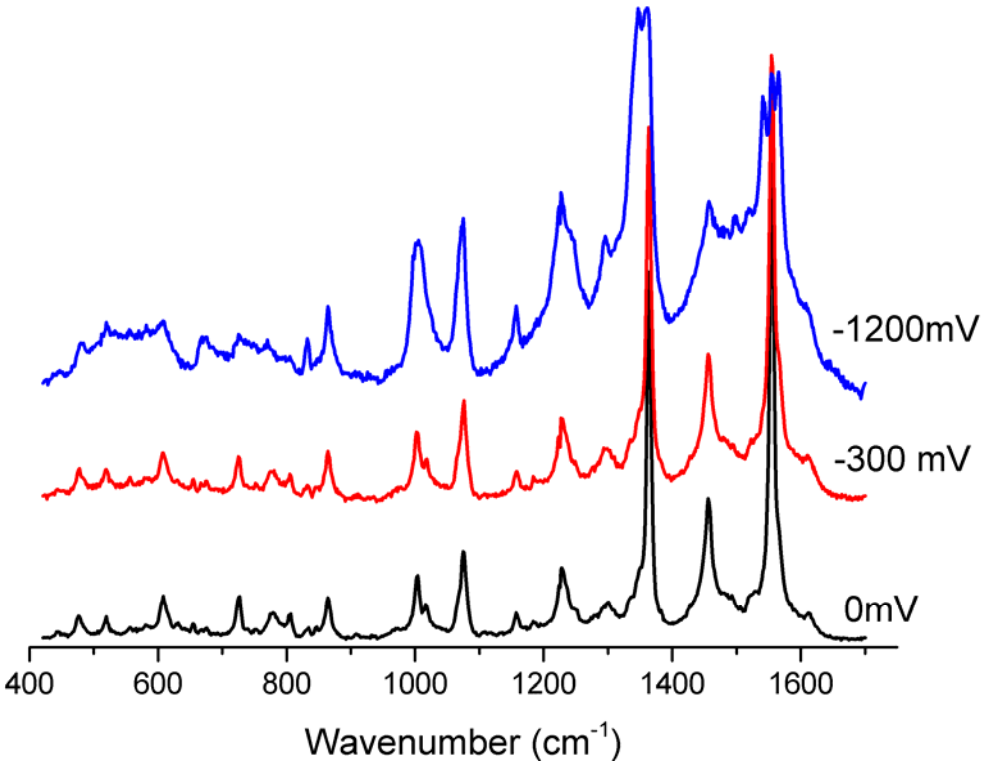

Figure S 3: Potential dependent SERR spectra of the iron Hangman complex immobilized on electrodes via drycast at 0 V and -1.2 V. Measurements were performed in air saturated pH 7 100 mM phosphate buffer, Potential vs. Ag/AgCl 3 M KCL Reference electrode.

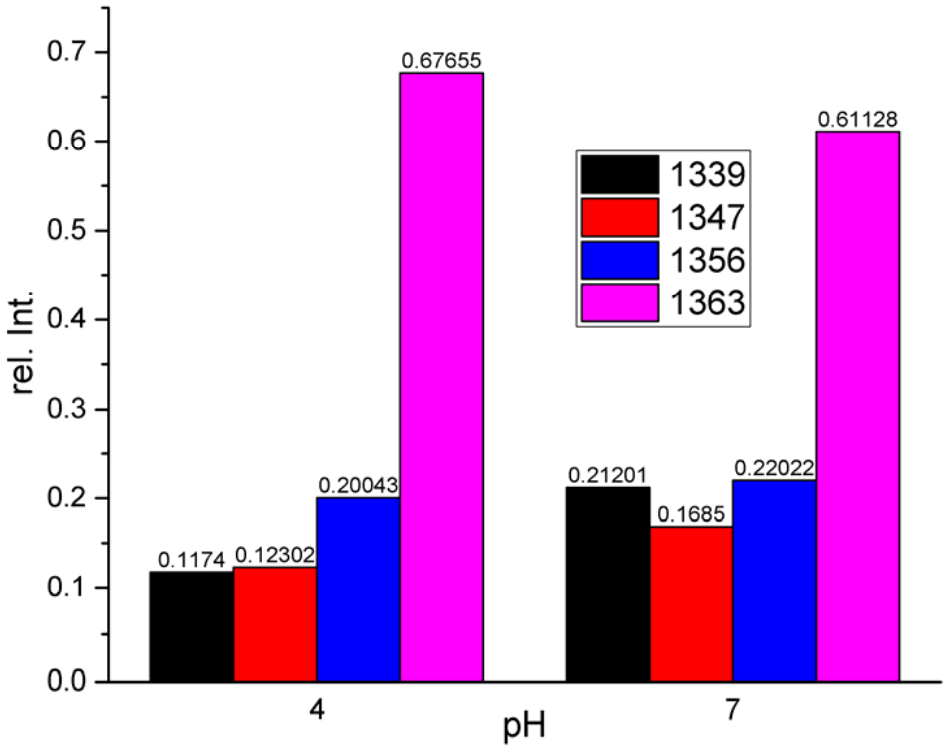

Figure S 4: Intensities of the bands at 1363 cm^{-1}, 1347 cm^{-1}, 1356 cm^{-1} and 1339 cm^{-1} as a function of pH at a potential at - 0.8 V with oxygen saturated buffer 100 mM phosphate solution. The relative intensities of the three ν_4 bands (1363 cm^{-1}, 1347 cm^{-1}, 1356 cm^{-1}) accumulate to 1. The relative intensity of the 1339 cm^{-1} band is in ratio to the sum of all ν_4 bands.