Electronic Supplementary Information

Stabilization and strong oxidizing properties of Ag(II) in a fluorine-free solvent

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Materials

Silver(I) sulfate (Sigma Aldrich, 99.999%), and 65% oleum (Sigma Aldrich, 99.99%) were used without further purification. 100% Sulfuric acid (99.99%, POCh) was twice distilled in subboiling quartz still to eliminate impurities, which otherwise influenced results to a large extent.

The solutions of < 100% H_2SO_4 were prepared from 100% H_2SO_4 and triply distilled water additionally purified by Millipore filters (18.2 MΩ cm^2). The oleums of a given concentration were prepared from 100% H_2SO_4 and 65% oleum. Concentrations of the acid and oleums were determined by conductometric titration of H_2SO_4 by 65% oleum. The precise concentration can be determined by using this procedure since conductivity of the acid is strongly dependent on its concentration with minimum of conductance at 100% H_2SO_4.[i] Obtained values were additionally confirmed by density measurements. Thelargest concentration of oleum used was 33% (corresponding to 140% H_2SO_4), as for higher oleum concentrations (40-65% i.e. concentrations of H_2SO_4 up to 180%) the position of the small anodic signal (which is overlapped with large O_2 evolution wave) could not be determined precisely.

All glassware was thoroughly cleaned prior to use with “piranha solution” (1:10 per volume of 30% H_2O_2 and 96% H_2SO_4, respectively) at 80 ^oC.

Electrochemical measurements

Electrochemical measurements were performed using three-electrode setup in thermostated electrochemical glass cell with two separated compartments. Cell was hermetic with inert gas constant flow through solution or above it. N6.7 Ar gas with pressure regulator and gas lines of corresponding purity were used for deareation of electrolyte solution. All joints for argon inlet and outlet were made of Teflon. FTO embedded in Teflon was used as working electrode. Electrode surface area exposed to the solution was A=0.04 cm^2. Platinum sheet of large surface

area >10 cm^2 was used as counter electrode. The electrode potentials was measured versus saturated silver(I) sulfate electrode in concentrated sulurfic acid $Ag/Ag_2SO_{4(sat)}/H_2SO_4$ (95%). All potentials are given versus this electrode. Electrochemical measurements were performed by using Solartron-Shlumberger 1287A potentiostat and 1260 frequency response analyzer, both controlled by CorrWare® by Scribner Associates. All measurements were carried out at 25 ^oC with temperature control provided by thermostat.

References

[i] H. E. Darling, *J. Chem. Eng. Data*, 1964, **9**, 421; R. Popiel, *J. Chem. Eng. Data*, 1964, **9**, 269.