Supporting Material to:

**Early stages of catalyst aging in the iridium mediated water oxidation reaction**


**Figure S1.** Kinetic plot in which the concentration of 1 dropcasted is depicted versus the logarithm of the observed current. A first order rate dependence in iridium was found.
Figure S2. EQCM experiment wherein the mass balance (top) and current density (bottom) are simultaneously followed as a function of applied potential in case of a 1 mM solution of 1 in 100 mM Na₂SO₄ (non-buffered) on a relatively rough gold EQCM electrode. The first scan is depicted in bold.
Figure S3. EQCM experiment wherein the mass balance (top) and current density (bottom) are simultaneously followed as a function of applied potential in case of a 1 mM solution of 1 in 100 mM Na$_2$HPO$_4$ on a gold electrode. The first scan is depicted in bold. Phosphate is an inhibitor of catalytic activity mediated by 1.
Figure S4. Iridium 4f, nitrogen 1s and chloride 2p XPS signals of 3 (red) and 1 (olive) powders. The lines indicate a binding energy of 61.4 eV for iridium, 399.8 for nitrogen and 197.1 for chloride. A trace of chloride was also observed in the sample of 1, even though chloride analysis of the same batch by elemental analysis did not show any chloride content.
Figure S5. Iridium 4f signal, nitrogen 1s signal and chloride 2p signal of glassy carbon (red), 3 deposited on glassy carbon (olive), 1 deposited on glassy carbon (purple), 1 deposited on glassy carbon after partial desorption in a blank Na$_2$SO$_4$ solution (blue) and 1 deposited on gold (green). Except for glassy carbon, in all cases a iridium binding energy of 62.2 eV was found, which is significantly different to both powders of 1 and 3 (61.4 eV) as well as iridium oxide (Ir$_2$O$_3$: 61.8 eV and IrO$_2$: 63.0 eV). The nitrogen 1s binding energy of the adsorbed samples is identical to that of the powders of 1 and 3, indicating that the NHC ligand is still intact. Chloride is not retained in the absorbed sample when starting from 3.
Figure S6. Iridium 4f XPS signals of IrCl₄ ⋅ x H₂O (red), Iridium(III) 2,4-Pentadionate (olive), iridium foil sputtered (purple), iridium foil calcined (blue) and calcined IrCl₃ ⋅ x H₂O (green) yielding binding energies of 60.7 eV for metallic iridium and 61.8 eV for Ir₂O₃. IrO₂ has a binding energy of 63.0 eV.
Figure S7. First derivative of the X-ray absorption at the iridium L\textsubscript{3} edge for selected reference complexes 1, 3, [IrCp*Cl]_2 and IrO\textsubscript{2} as well as DM|GC prepared at 1.1 V, 1.3 V, 1.5 V, 1.7 V, 1.9 V and 2.0 V versus RHE.