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Evaluation of Iron-based electrocatalysts for water oxidation – an on-line mass spectrometry approach†

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Using on-line mass spectrometry in combination with classical electroanalytical techniques makes it possible to reliably determine onset potentials and to distinguish between competing reactions such as oxygen evolution and carbon dioxide formation. Using these on-line MS methods, catalytic water oxidation activity was demonstrated for *cis*-[Fe(cyclam)Cl₂]Cl (1) and [Fe(cyclamacetate)Cl] (2).

In order to move away from a society which heavily depends on fossil fuels, new means of harvesting and storing energy are required. Amongst the available sustainable energy sources, solar radiation is the only source of energy that can be harvested in sufficient amounts to meet global demands.¹ To become independent of location, daytime and weather, the energy captured from sunlight is preferably converted to chemical energy in the form of a fuel, which can be stored, shipped and combusted as required. Over the last few decades, considerable effort has been made to split water in order to produce environmentally friendly hydrogen as a green and sustainable energy carrier. Within this process, it is especially the water oxidation reaction that is very challenging. A better fundamental understanding is needed in order to develop new catalysts which preferably consist of abundant materials – rather than e.g. ruthenium or iridium – and operate with high catalytic rates at low overpotentials.²

Iron-based catalysts are among the most interesting candidates for such development due to the high abundance and low toxicity of iron. The molecular iron catalysts reported so far³ do not perform as well as their less abundant iridium and ruthenium counterparts.⁴ The turnover numbers rarely exceed a hundred turnovers and Faradaic efficiencies – if available – are generally low. For the systems which were studied electrochemically, the recorded overpotentials generally exceed 500 mV.

So far, most of the research on molecular iron catalysts has

been carried out using sacrificial electron acceptors such as cerium(IV) ammonium nitrate and sodium periodate.^{3b-f} These sacrificial agents are notorious as they may not necessarily react via the anticipated innocent one-electron transfer pathways. Recently, several reports were published in which oxygen atom transfer pathways have been proposed and identified.⁵ Hence in this study we propose electroanalytical techniques to study the activity of water oxidation catalysts. By combining classical electrochemical methods such as cyclic voltammetry and amperometry with on-line mass spectrometry, we gain access to real-time information about gaseous products being formed at the electrode surface, allowing for the precise assessment of the onset of oxygen evolution as well as certain decomposition pathways.

Although iron-based catalysts featuring vacant sites in *trans*-configuration – like the iron-TAML complexes by Collins et al.⁶ – have been designed and established, recent mechanistic studies have shown that two vacant coordination sites in *cis*-configuration are beneficial for obtaining decent catalytic rates in case of molecular iron-based catalysts.^{3b} Subsequent DFT calculations support this claim and suggest that water oxidation occurs via a nucleophilic attack of water on a high-valent iron(V) oxo species with another oxo moiety in *cis*-position acting as an internal base, facilitating the rate-limiting O-O bond formation.⁷ Yet other publications point to the direct involvement of sacrificial reagents in the catalytic reaction.^{5g} Intrigued by these findings we investigated a selection of iron-catalysts with different structural motifs by means of electroanalytical techniques.

Despite their possibly limited stability under highly oxidative conditions, macrocyclic cyclam-based ligands (Fig. 1) were selected in this study for complexation to iron because i) such complexes are expected to be relatively stable towards ligand dissociation and ii) corresponding iron complexes bearing vacant sites in *cis*- and *trans*-position have been synthesized⁸ and used in oxidation chemistry⁹ previously. Whereas we do not find considerable catalytic activity in case of *trans*-[Fe(cyclam)Cl₂] (3), the complexes *cis*-[Fe(cyclam)Cl₂]Cl (1) and [Fe(cyclamacetate)Cl] (2) are capable

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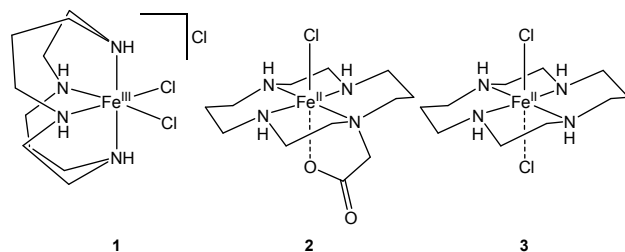


Fig. 1 The structures of complexes 1, 2 and 3

of catalyzing the water oxidation reaction. To the best of our knowledge, [Fe(cyclamacetate)Cl] (**2**) is the first iron-based water oxidation electrocatalyst with only one free coordination site which is active in aqueous media.^{3a}

Cis-[Fe(cyclam)Cl₂]Cl (**1**) was synthesized according to literature procedures.^{8a} We isolated the complex as orange crystals of high purity, which was confirmed by elemental analysis. Whereas complex **1** was obtained as a Fe^{III} species, the complexes **2** and **3** were isolated as Fe^{II} species and oxidized to the Fe^{III} species *in situ*.

Complex **2** can be isolated as a white powder and air-free solutions of **2** in acetonitrile, water and methanol are colourless, all of which is in agreement with a high-spin Fe^{II} configuration. Upon exposure to air, solutions of complex **2** instantly turn (dark) yellow indicating oxidation from Fe^{II} to Fe^{III}. EPR-measurements indicate that complex **2** is EPR-silent (X-band), which is not uncommon for iron(II) high-spin species.¹⁰ After exposure of the aqueous solution to air at room temperature, the oxidized complex yields an EPR spectrum with three distinct *g*-values of 2.48, 2.21 and 1.89 (Fig. S1a) which is in good agreement with previous reports.¹¹ For the the C=O stretch vibration of the carboxyl group, a shift of 139 cm⁻¹ can be observed by comparing the IR spectra of the ligand and complex **2**, suggesting that the acetate group coordinates to the iron-centre in the solid state (Fig. S2).

The Fe^{III} *trans*-analogue of complex **1** has been reported previously.^{8a} However, the complex was isolated as a [FeCl₄]⁻ salt and recrystallization with other counter-ions proved to be difficult. To avoid the presence of any [FeCl₄]⁻ in the catalytic experiments a different approach was taken. *Trans*-[Fe(cyclam)Cl₂] (**3**) was synthesized as the Fe^{II} species in a procedure analogous to that of complex **2** and was isolated as a light pink powder.

Previous reports show that the iron-centre in complex **1** is a high-spin Fe^{III} site whereas the analogous *trans*-species has a low-spin Fe^{III} centre due to Jahn-Teller distortion.^{8a} The EPR spectrum obtained for the oxidized form of complex **3** shows the presence of high and low-spin Fe^{III} species (Fig. S1b). The predominant signal shows *g*-values of 2.38, 2.23 and 1.92, which are very similar to those of the oxidized form of complex **2**. This suggests that the major species present in solution has a similar electronic structure to the oxidized form of complex **2**, indicating the desired *trans*-configuration.

The redox behaviour and catalytic activity of *cis*-[Fe(cyclam)Cl₂]Cl (**1**), [Fe(cyclamacetate)Cl] (**2**) and *trans*-

[Fe(cyclam)Cl₂] (**3**) were carefully studied via electroanalytical techniques using a pyrolytic graphite (PG) working electrode in aqueous solutions of either unbuffered 0.1 M NaClO₄ or 0.1 M phosphate buffer (pH 7.5).¹² Experiments using FeCl₂ under identical conditions revealed that the presence of the cyclam ligands is indeed required to achieve catalytic activity. Electrochemical experiments using acidic media (pH 1) yielded poor results and preliminary tests with chemical oxidants showed only low single digit turnover numbers and rapid catalyst deactivation. We refrained from catalytic studies under very alkaline conditions to avoid formation of iron oxide which could potentially obscure catalytic activity of the molecular complexes.¹³ To investigate whether the catalytic results depend on the electrode of choice,¹⁴ we tested several different electrode materials and eventually selected PG as the best material for our purposes.¹⁵

To identify the products formed upon electrochemical oxidation and to reliably determine the onset potentials of these reactions, online electrochemical mass spectrometry (OLEMS) was used. In OLEMS measurements, the *m/z* traces for selected gaseous products, sampled close to the electrode surface in solution, are recorded during electrochemical measurements.¹⁶ In all electrochemical experiments discussed in this report, complex **1** was used directly as the isolated Fe^{III} species. Complexes **2** and **3** were oxidized *in situ* to the corresponding Fe^{III} species by dissolving them in air-saturated electrolyte solution and subsequently added to the electrochemical cell. Control experiments in which complexes **2** and **3** were added directly as the Fe^{II} species revealed that – as expected – the *in situ* oxidation to the Fe^{III} state does not affect the catalytic results.

In an unbuffered 0.1 M NaClO₄ solution, complex **1** shows a reversible wave at 0.7 V vs. RHE which was assigned to the Fe^{II/III} couple (Fig. 2a). Starting at 1.7 V, a sharp increase in current can be observed in the voltammogram (Fig. 2b, S3). In chronoamperometry measurements at 1.9 V, immediate O₂ evolution was detected via OLEMS, without any induction period or any CO₂ formation preceding the onset of O₂ evolution (Fig. 2c). This indicates that the catalytic reaction is indeed mediated by a molecular species. The profile of the O₂ evolution is very similar to that commonly observed in experiments in which sacrificial oxidants were used to drive water oxidation and the evolved O₂ was measured with a Clark-type oxygen sensor.^{6b} The mass trace of O₂ was also measured as a function of potential to determine the onset potential for O₂ evolution. Following the recorded traces for *m/z* = 32 (Fig. 2b), an increase in signal can be observed indicating the formation of dioxygen starting at 1.7 V. Additionally, the trace of *m/z* = 44 was measured to follow the formation of CO₂ which we expect to be a product of oxidative decomposition of the ligand framework. Comparison of the mass traces shows that the formation of CO₂ starts at lower potentials than the evolution of O₂ (Fig. 2b). The formation of CO₂ points to a weakness of the ligand framework under these oxidizing conditions. This finding is in line with the results of previous reports of iron-based molecular catalysts for water

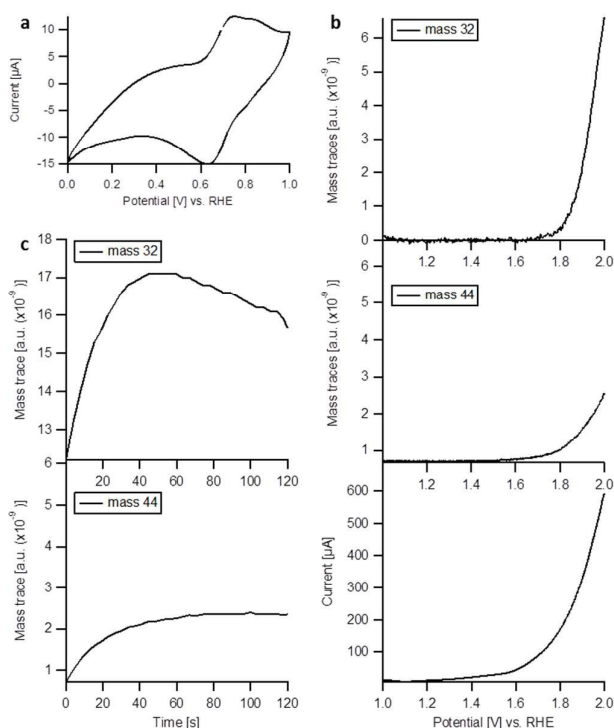


Fig. 2 Results of electrochemical experiments of complex **1** in 0.1 M NaClO₄ solution using a PG working electrode. (a) Voltammogram showing the reversible wave assigned to the Fe^{II/III} couple at a scan rate of 10 mV/s (b) Forward scan of an OLEMS measurement showing the m/z trace for O₂ (top), m/z trace for CO₂ (middle) and corresponding current (bottom). (c) The m/z traces of O₂ (top) and CO₂ (bottom) recorded during chronoamperometry measurement at 1.9 V vs. RHE.

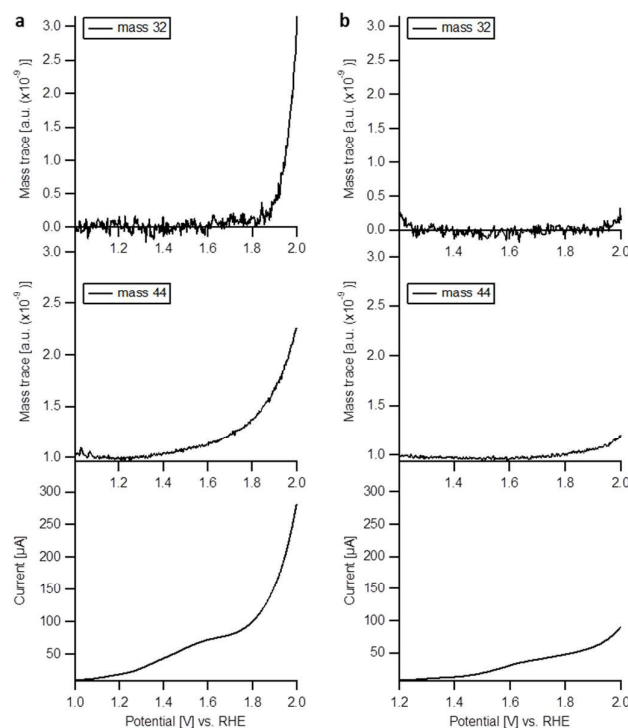


Fig. 3 Comparison of OLEMS measurements in 0.1 M NaClO₄ solution using a PG working electrode for (a) complex **2** and (b) complex **3**. Shown are the forward scans of a CV experiment with the m/z trace for O₂ (top), m/z trace for CO₂ (middle) and corresponding current (bottom).

oxidation which generally show low Faradaic efficiencies or low turn-over numbers.^{3b, 3c, 3i} It has to be noted that the observed CO₂ may originate at least in parts from oxidation of the carbon electrode itself, mediated by the presence of high-valent iron oxo-species. To get further insight into the catalyst stability, we performed cyclic voltammetry of complex **1** followed by chronoamperometry for 180 s at 1.9 V vs. RHE immediately followed by another cyclic voltammetry run, starting with a cathodic scan from 2 V to 0 V vs. RHE. The voltammogram recorded before and after chronoamperometry are almost superimposable, except for an increase in reductive current between 0.5 V and 0.0 V vs. RHE (Fig. S4-S6), which most likely stems from the reduction of the oxygen produced during the chronoamperometry experiment. We expect that diffusion of unreacted complex from the bulk solution to the electrode surface will mask the effect of catalyst decomposition to some extent. However, from these results the catalyst appears to be reasonably stable within the time span of our experiments.

Similar to complex **1**, complex **2** shows a reversible Fe^{II/III} redox-couple at 0.7 V (Fig. S7). Starting at 1.3 V, an irreversible oxidative current can be observed in the voltammogram with a sharp increase in current starting at 1.8 V (Fig. 3a, S8). Chronoamperometry measurements at 2.0 V again show immediate O₂ evolution without any sign of an induction period or CO₂ formation preceding the evolution of O₂ (Fig. S9). Measuring the mass trace of O₂ as a function of potential shows that the onset of O₂ evolution correlates with the sharp increase in oxidative current at 1.8 V (Fig. 3a). The current

observed between 1.3 and 1.8 V correlates with CO₂ formation (Fig. 3a). The reversible Fe^{II/III} couple of complex **3** was observed at 0.9 V in a NaClO₄ solution (Fig. S10). From 1.5 V onwards an irreversible oxidative current can be observed with a sharp increase at 1.9 V. In the OLEMS measurements, detectable amounts of CO₂ are observed beyond 1.6 V and the irreversible oxidative current starting at 1.9 V can be attributed to O₂ evolution (Fig. 3b, S11). Based on these results, it appears that the catalytic activity for complex **3** is substantially lower compared to **1** and **2**. Considering the presence of some high-spin Fe^{III} species in aqueous solutions of **3** (Fig. S1b), one might wonder whether the *trans*-complex is active at all or whether the observed catalytic activity for **3** is merely an artefact, due to small amounts of *cis*-complex present in solution.

For applications of a catalytic system at neutral pH, it is relevant whether the catalyst is active in the presence of a pH buffer. Both complexes **1** and **3** are fully deactivated in phosphate containing media. Both complexes show a cathodic shift of the Fe^{II/III} redox couple to 0.3 V vs. RHE (Fig. S12, S13), indicating a strong interaction with phosphate. OLEMS measurements of complex **1** show the same CO₂ formation profile as seen previously in an unbuffered NaClO₄ solution but no signs of O₂ evolution up to 2.0 V (Fig. S14). At low scan rates (1 mV/s) and in the presence of phosphate, complex **3** forms a deposit of an unidentified blue material on the surface of the PG electrode (Fig. S15). The blue deposit itself is active for water oxidation (Fig. S16, S17), albeit with an onset for O₂ evolution above 1.9 V. In the presence of 0.1 M phosphate (pH 7.5), complex **2** shows redox couples at 0.3 V and 0.6 V,

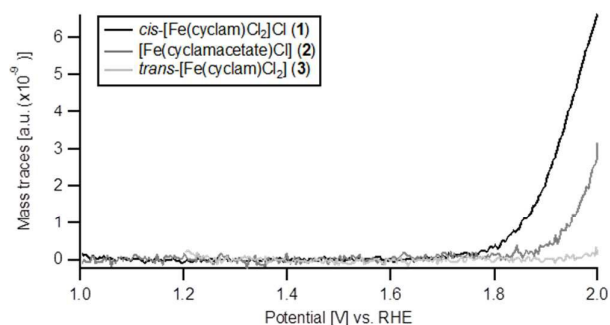


Fig. 4 Comparison of the O_2 traces ($m/z = 32$) for complexes **1**, **2** and **3** recorded via OLEMS in cyclic voltammetry mode in 0.1 M $NaClO_4$ solution using a PG working electrode (c.f. Fig. 2b and 3).

indicating only partial inhibition by phosphate. (Fig. S18). An onset for O_2 evolution was observed at 1.9 V (Fig. S19). In contrast to complex **3**, complexes **1** and **2** showed no visible signs of deposition of (blue) material onto the electrode surface even after prolonged potential cycling between 1 and 2 V at a scan rate of 1 mV/s. Electrodes which were taken out of a phosphate buffer solution containing complex **1** or **2**, rinsed with Milli-Q water and placed in a fresh phosphate buffer solution of identical concentration and pH did not produce any additional current above the PG background.

In conclusion, the results of our study show that water oxidation activity of iron complexes can be enabled both by the motif of *cis* vacant sites as well as a fifth donor ligand in axial position.

While *cis*-[Fe(cyclam)Cl₂]Cl (**1**) displays water oxidation activity which corresponds well with the results previously reported for comparable molecular iron-based catalysts,^{3a, 3i, 3j} complex **2** is the first water oxidation catalyst of its kind to operate in aqueous media. Despite its somewhat lower initial activity compared to complex **1**, complex **2** appears to be more tolerant towards the presence of a buffer.

The use of on-line mass spectrometry techniques allows us to differentiate between catalytic current and current caused by decomposition of the catalyst. Furthermore, using this technique we can reliably determine the onset potential for water oxidation and compare the efficiency of different catalysts in terms of overpotential (Fig. 4). We believe that this technique offers valuable new insight for studying water oxidation activity and helps to alleviate some of the ambiguity caused by sacrificial chemical oxidants.

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