A fluorescence-based screening protocol for the identification of water oxidation catalysts

Detz, R.J.; Abiri, Z.; Kluwer, A.M.; Reek, J.N.H.

DOI
10.1002/cssc.201500558

Publication date
2015

Document Version
Final published version

Published in
ChemSusChem

License
Article 25fa Dutch Copyright Act

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (https://dare.uva.nl)
A Fluorescence-Based Screening Protocol for the Identification of Water Oxidation Catalysts

Remko J. Detz,[a] Zohar Abiri,[a, b] Alexander M. Kluwer,[b] and Joost N. H. Reek*[a]

Efficient catalysts are crucial for the sustainable generation of fuel by splitting water. A versatile screening protocol would simplify the identification of novel and better catalysts by using high throughput experimentation. Herein, such a screening approach for the identification of molecular catalysts for chemical oxidation of water is reported, which is based on oxygen-sensitive fluorescence quenching using an OxoDish. More than 200 reactions were performed revealing several catalysts, for example, a dinuclear Fe complex that produced oxygen under the used reaction conditions. Clark electrode measurements confirmed a similar rate in oxygen evolution, making the developed parallel screening approach a robust and versatile tool to screen for molecular water oxidation catalysts using chemical oxidants under acidic and neutral conditions.

Introduction

The development of efficient processes to generate chemical fuels using sunlight as primary energy source can significantly contribute to the total energy demand and diminish our dependence on fossil fuels and nuclear power. The light-driven water splitting reaction to generate molecular hydrogen and oxygen is one of the most promising processes for producing a clean fuel, and catalysis plays a crucial role to facilitate this. For water splitting in a photoelectrochemical (PEC) cell, the two half reactions, water oxidation (anode side) and proton reduction (cathode side), both require their own specialized catalysts. Molecular catalysts can be tailored both structurally and electronically by modifying the ligand and can be studied mechanistically using various spectroscopic techniques, which give them an advantage over heterogeneous systems. Despite the extensive research conducted by the scientific community, only a relatively small number of molecular water oxidation catalysts is known to date.[1] The lack of structure–activity relationships and detailed mechanistic insight makes the rational design of (molecular) water oxidation catalysts that work at low overpotential while displaying a fast catalysis combined with high stability a difficult task.

High throughput screening (HTS) techniques[2] are widely applied in the field of catalysis and facilitate the identification of new and possibly better water oxidation catalysts. A particular difficulty for setting up a HTS system for water oxidation is that the critical observable parameter, the reaction product, is molecular oxygen. Most typical chemical HTS equipment is not suitable for monitoring oxygen-producing reactions or have a high propensity of false positive results (e.g., due to detection of other gasses such as CO₂ when using pressure sensors), which limits the amount of reactions that can be performed tremendously. To speed up the development of water oxidation catalysts, there is a need for a reliable and fast lead-finding method that allows the evaluation of large numbers of catalysts. The leads found should subsequently be analyzed further and characterized by more standard experiment techniques, such as electrochemistry, Clark electrode analysis,[3] headspace analysis using gas chromatography, and/or the use of pressure sensors,[1,4] that are much more laborious and/or expensive to perform. A few combinatorial approaches have been reported to screen a variety of anode materials, mainly metals and metal oxides, for the electrochemical oxidation of methanol and water by making use of indicators,[5] a pH-sensitive fluorescent indicator dye,[6] detection of bubble formation,[7] electrochemical techniques,[8] or an oxygen-sensitive fluorescence-quenching assay.[9] Herein, we present a new screening approach based on oxygen-sensitive fluorescence quenching for the chemical oxidation of water that is especially designed for molecular catalysts. For this, the commercially available OxoDishes are used, which are 24-well microplates equipped with optical oxygen sensors integrated at the bottom of each well and which are currently only used to study the growth of algae and bacteria by monitoring the oxygen content. These sensors can be read out using a SensorDish Reader (see Figure 1).[10] The sensor contains an oxygen-sensitive indicator dye, which is immobilized in a thin polymer film. The phosphorescence is quenched by the presence of oxygen, and the shortened phosphorescence life time of the dye is thus an indicator for the amount of oxygen present in the solution.

[a] Dr. R. J. Detz, Z. Abiri, Prof. Dr. J. N. H. Reek
Van’t Hoff Institute for Molecular Sciences
University of Amsterdam
Science Park 904
1098 XH Amsterdam (The Netherlands)
E-mail: j.n.h.reek@uva.nl

[b] Z. Abiri, Dr. A. M. Kluwer
InCatT B.V.
Science Park 904, 1098 XH Amsterdam (The Netherlands)

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201500558.
In principle, the chemical oxidants also oxidize solutions (blue lines) and these catalysts were also identified as active catalysts after no oxygen evolution was observed. Remarkably, using the buffered and unbuffered (CAN, ruthenium(III) tris(bipyridine) and iridium(pentamethylcyclopentadienyl)dichloride ([IrCp*(NHC)Cl]) complex 1; see Figure 3), which is known to oxidize water using either cerium ammonium nitrate (CAN) or sodium periodate as chemical oxidants. The OxoDish wells were filled with solutions of CAN and NaIO₅ (buffered and unbuffered) prepared in double-distilled water. A catalyst solution in water was carefully added while measuring the oxygen levels in solution. Each OxoDish well was filled with 1.2 mL reaction mixture after which the full OxoDish was covered with a seal to prevent gas diffusion. Control experiments, that is, OxoDish wells containing only the buffered chemical oxidant solution showed no increase in oxygen levels whereas reaction wells containing catalyst 1 displayed a continuous increase of the oxygen concentration (Figure 4).

Depending on the catalyst concentration, the oxygen levels increased very rapidly, reaching the maximum detection value within a few data points, or slower, demonstrating that the oxygen production depends on catalyst concentration. The continuous monitoring of oxygen formation makes our methodology ideal for fast lead finding. Thus, in addition to the discovery of a new potential catalyst an estimation of the relative rate is also provided. Further studies using, for example, a Clark electrode, stop-flow kinetics, and electrochemistry can be used to optimize the reaction conditions and study the catalyst in more detail.

To validate the method, four benchmark water oxidation catalysts (WOCs; 1, 2, 3, and 4), were selected (Table 1). Ru complex 2 showed an extremely fast increase in the oxygen level, and within 15 s (one data point) the solution was saturated with oxygen (Table 1, entry 2); this confirms its very high activity for water oxidation using CAN. Remarkably, using the two-electron oxidant NaIO₅ no oxygen evolution was observed. The complete inactivity of 2 using NaIO₅ underlines the need to screen various chemical oxidants to not overlook a potential catalyst lead and to identify which catalysts have an activity that is sensitive to the chemical oxidant.

One of the most promising Fe-based WOCs, reported by Filol et al., are the iron triflate (OTf) or chloride (Cl) complexes bearing the tetradeinate nitrogen ligand \( N'N' '-\text{bis}(2\text{-pyridylmethyl})\text{-cyclohexane-1,2-diamine} \) (mpc) [Fe(OTf)₃(mpc)] and [Fe(Cl)₃(mpc)] (complexes 3 and 4, respectively). These catalysts were also identified as active catalysts under the applied reaction conditions (see Table 1, entries 3 and 4); this confirms that all four already known WOC catalysts were positively identified within the OxoDish method and
both chemical oxidants cerium ammonium nitrate and sodium periodate were appropriate oxidants. Next, we set out to screen for new WOC catalysts and we performed over 200 reactions in the OxoDish examining various metal complexes (unknown for water oxidation catalysis) using different chemical oxidants and different pH values (Table 2). During screening, oxygen was detected for all tested Ir- and Ru-based complexes (entries 1–6, and the Supporting Information). The relative rate of oxygen evolution allows the comparison of catalyst activity and shows that Ir catalyst 1 and Ru catalyst 2 are among the fastest tested WOC catalysts so far. However, when considering the eventual incorporation into a water splitting device, less expensive and more readily available transition-metal catalysts based on first row transition metals are preferred. Therefore, for the remainder of the catalyst screening, we particularly focused on Fe-based water oxidation catalysts due to the use of the inexpensive, readily available metal.

As already described above, the Fe-based catalysts 3 and 4 (entries 7–10) formed oxygen under the applied reaction conditions. The closely related complexes 8–11 were also active, particularly when the one-electron oxidant cerium ammonium nitrate was used as chemical oxidant. The catalyst library was extended with other, closely related iron catalysts, and it was found that small changes in the ligand structure completely changed the activity of the catalysts (Figure 5 and also the Supporting Information). Changing the cyclohexyl backbone for an aromatic ring (4 vs. 8) resulted in only slightly lower activities, probably due to lower electron density on the Fe center. The small substituent on the two nitrogen atoms had a huge effect on the activity: methyl groups were optimal (4), ethyl moieties were tolerated (10), but lower activity was observed, and the catalyst with free NH functional groups (11) displayed very poor activity. Changing the methylene spacer for an amide linkage completely deactivated the catalyst (18). These findings can help to understand the structure–activity relationship for this type of ligands, which facilitates the optimization of these catalysts.

In addition to the complexes analogous to benchmark WOCs, some new leads were found that revealed activity. Under neutral conditions both the Fe–ethylenediaminetetraacetic acid (EDTA) complex 12 and the Cu–EDTA complex 15 demonstrated a low but significant increase in the oxygen concentration, reaching their maximum level after 1 h reaction time. Also, the dinuclear Fe complexes 13 and 14 were active oxygen evolution catalysts when using NaIO₄ as the chemical oxidant. Although these complexes are less active as the benchmark Fe complex 3, the increase in oxygen level, even after almost 2 h reaction time, indicates that the stability is
good, which makes these complexes interesting for further optimization. Also, for the Ni complex 16, and the Co complex 17 a modest increase in the oxygen level was detected. More experiments are required to confirm the water oxidation properties of these complexes. For complex 13, we confirmed the water oxidation activity by performing Clark electrode experiments that showed similar rates of oxygen formation (see Figure 6). This shows that the OxoDish can even be used to study the rate (and thus kinetics) of the reaction under certain reaction conditions, revealing the versatility of this parallel reaction and analysis tool. All leads found using the screening protocol are currently under further investigation.

Conclusions

We demonstrated in this contribution that the OxoDish provides a robust and versatile tool for the parallel screening of soluble metal complexes for water oxidation activity using chemical oxidants under acidic and neutral conditions. After validation of the

Table 2. Selection of screening results for WOCs in the OxoDish.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex (metal)</th>
<th>Ratio oxidant/complex</th>
<th>Activity ([O_2]^{2+} [\text{ min}]) CAN</th>
<th>NaIO(_4)</th>
<th>NaIO(_4) at pH7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ir</td>
<td>50</td>
<td>2</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>2</td>
<td>Ir</td>
<td>1000</td>
<td>17</td>
<td>10 – 25</td>
<td>10 – 25</td>
</tr>
<tr>
<td>3</td>
<td>Fe</td>
<td>500</td>
<td>60</td>
<td>60 – 120</td>
<td>60 – 120</td>
</tr>
<tr>
<td>4</td>
<td>Fe</td>
<td>250</td>
<td>40</td>
<td>40 – 80</td>
<td>40 – 80</td>
</tr>
<tr>
<td>5</td>
<td>Fe</td>
<td>1000</td>
<td>10</td>
<td>10 – 60</td>
<td>10 – 60</td>
</tr>
<tr>
<td>6</td>
<td>Fe</td>
<td>250</td>
<td>5</td>
<td>5 – 15</td>
<td>5 – 15</td>
</tr>
<tr>
<td>7</td>
<td>Fe</td>
<td>1000</td>
<td>3</td>
<td>3 – 15</td>
<td>3 – 15</td>
</tr>
<tr>
<td>8</td>
<td>Fe</td>
<td>250</td>
<td>1</td>
<td>1 – 5</td>
<td>1 – 5</td>
</tr>
<tr>
<td>9</td>
<td>Fe</td>
<td>500</td>
<td>2</td>
<td>2 – 5</td>
<td>2 – 5</td>
</tr>
<tr>
<td>10</td>
<td>Fe</td>
<td>1000</td>
<td>4</td>
<td>4 – 15</td>
<td>4 – 15</td>
</tr>
<tr>
<td>11</td>
<td>Fe</td>
<td>250</td>
<td>6</td>
<td>6 – 20</td>
<td>6 – 20</td>
</tr>
<tr>
<td>12</td>
<td>Fe</td>
<td>500</td>
<td>8</td>
<td>8 – 30</td>
<td>8 – 30</td>
</tr>
<tr>
<td>13</td>
<td>Fe</td>
<td>250</td>
<td>10</td>
<td>10 – 30</td>
<td>10 – 30</td>
</tr>
</tbody>
</table>

[a] Amount of oxidizing equivalents; the concentration of the chemical oxidant (0.1 M in CAN, 0.05 M in NaIO\(_4\)) is kept constant in all experiments, only the amount of catalyst is varied. [b] The color indicates the amount of maximum measured \([O_2]^{2+}\) concentration: red (high) = > 650 nmol mL\(^{-1}\); orange (medium) = 381–650 nmol mL\(^{-1}\); yellow (low) = 270–380 nmol mL\(^{-1}\); no color = < 270 nmol mL\(^{-1}\). The number is the time in minutes in which the maximum \([O_2]^{2+}\) concentration is reached.
 Experimental Section

Typical OxoDish experiment: a freshly unpacked OxoDish 24-well sensorplate (OD24) was placed on the SensorDish Reader. The wells (3 mL) were filled with aqueous solutions of the chemical oxidant (typical 1 mL of 0.12 m oxidant) and left for roughly 15 min to equilibrate. Next, the solution of catalyst (dissolved in double-distilled water with [if required] some acetonitrile added to dissolve the catalyst; typical 0.2 mL of 0.3 mM catalyst) was gently added to avoid disturbing the sensor response. Control experiments were performed by adding similar solutions without the catalyst (or oxidant). After finishing the additions, the plate was capped with a plastic seal.

OxoDish versus Clark electrode: to test the similarity between the OxoDish and the Clark electrode measurements, the protocol used for the screening was copied for the Clark electrode setup. After calibration of the Clark electrode (using air- and nitrogen-saturated water), the chamber was filled with the NaOH solution in phosphate buffer (1.67 mL, 0.06 M, pH 7). After stabilization (5 min), the catalyst solution in water (0.33 mL, 0.5 mM) was added and the chamber was capped.

Data of the full screening are available in the Supporting Information.

Acknowledgements

The following people are acknowledged for providing metal complexes that were screened: R. Becker, T. Bouwens, M. van den Brink, D. G. H. Hetterscheid, E. Jansen, J. M. Koelewijn, M. Schaveling, T. van Schayk, F. Terrade, and A. Wolters. This project was carried out within the research programme of BioSolar Cells, co-financed by the Dutch Ministry of Economic Affairs.

Keywords: high-throughput screening - homogeneous catalysis - iron - oxygen evolution - water oxidation.