Published in final edited form as:

Dalton Trans. 2017 January 31; 46(5): 1382–1388. doi:10.1039/c6dt03718f.

Electrocatalytic Water Oxidation by a Molecular Catalyst Incorporated into a Metal-Organic Framework Thin Film

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Abstract

A molecular water oxidation catalyst, $\text{Ru}(\text{tpy})(\text{dcbpy})\text{OH}_2(\text{ClO}_4)_2$ (tpy = 2,2':6',2''-terpyridine, dcbpy = 2,2'-bipyridine-5,5'-dicarboxylic acid) [1], has been incorporated into FTO-grown thin films of UiO-67 (UiO = University of Oslo), by post-synthetic ligand exchange. Cyclic voltammograms (0.1 M borate buffer at pH = 8.4) of the resulting UiO67-[RuOH₂]@FTO show a reversible wave associated with the $\text{Ru}^{\text{III/II}}$ couple in the anodic scan, followed by a large current response that arises from electrocatalytic water oxidation beyond 1.1 V *vs.* Ag/AgCl. Water oxidation can be observed at an applied potential of 1.5 V over the timescale of hours with a current density of 11.5 $\mu\text{A cm}^{-2}$. Oxygen evolution was quantified in-situ over the course of the experiment and the Faradaic efficiency was calculated as 82%. Importantly, the molecular integrity of [1] during electrocatalytic water oxidation is maintained even on the timescale of hours under turnover conditions and applied voltage, as evidenced by the persistence of the wave associated with the $\text{Ru}^{\text{III/II}}$ couple in the CV. This experiment highlights the capability of metal organic frameworks like UiO-67 to stabilize the molecular structure of catalysts that are prone to form higher clusters in homogenous phase.

Introduction

In order to meet future energy needs, the conversion of solar energy into clean and renewable chemical fuels will undoubtedly require splitting water into molecular oxygen and protons, while transferring the necessary reducing equivalents to produce a fuel (H_2 , CO, COOH, CH_3OH , CH_4).^{1–4} The photo- or electrochemical oxidation of water (oxygen evolution reaction, OER) is kinetically demanding, due to the transfer of 4e^- and 4H^+ and the formation of the oxygen-oxygen bond, and therefore requires a catalyst to facilitate higher rates at lower overpotentials.⁵ Many homogenous, molecular, transition metal-based catalysts, have been found to efficiently oxidize water;^{5–7} however, such systems are often plagued under particular reaction conditions by issues with stability and the formation of nano-particles, which frequently are also active towards water oxidation.^{8–10} These factors limit activity and add ambiguity to the mechanism and to the characterization of the active catalyst.

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Metal-organic frameworks (MOFs) are a class of coordination polymers that exhibit high porosity and crystallinity, highly ordered internal pores, and large surface areas.¹¹ In addition, MOFs show promising applications towards catalysis due to the modular nature of their structure, consisting of organic linkers and inorganic nodes.^{12, 13} These components can be substituted with catalytically active functionalities, for example a transition-metal complex, either directly during solvothermal synthesis^{14–16} or *via* post-synthetic exchange (PSE),^{17–19} where the organic linkers are replaced by matching sized complexes bearing the same binding group.²⁰ Stabilization of metal complexes which act as catalysts for solar fuel transformations in MOFs²¹ has been reported for water oxidation,^{14, 22–27} CO₂ reduction,^{18, 19, 28–30} and proton reduction.^{17, 31, 32}

Following this strategy, we chose to incorporate a well-known water oxidation electrocatalyst^{33–37} functionalized with carboxylic acid groups, Ru(tpy)(dcbpy)OH₂] (ClO₄)₂ (tpy = 2,2':6',2''-terpyridine, dcbpy = 2,2'-bipyridine-5,5'-dicarboxylic acid) [**1**], into UiO-67 (UiO = University of Oslo),³⁸ a stable (even under OER conditions),¹⁴ robust framework made from Zr₆(O)₄(OH)₄ metal clusters connected with biphenyl-4,4'-dicarboxylic acid (bpdc) linkers (Scheme 1). UiO-67 was grown directly onto a conductive substrate (FTO), and [**1**] was incorporated into the framework under mild conditions by PSE. The resulting MOF thin films were characterized and examined by electrochemical methods. In addition, we have determined the electrocatalytic water oxidation activity of the film during OER. The results herein are one of the first examples of catalytic water oxidation by an electroactive molecular complex incorporated in a MOF grown directly onto a functional electrode.³⁹

Experimental Section

Materials

All solvents and commercially supplied chemicals were reagent grade and used as received without further purification. ZrCl₄ (99.99%), biphenyl-4,4'-dicarboxylic acid (bpdc) (97%), 2,2':6',2''-terpyridine (tpy) (98%), 4-ethylmorpholine (97%), 5,5'-dimethyl-2,2'-bipyridine (98%), Nafion (10 wt. % in H₂O), AgClO₄, LiCl, and HClO₄ were purchased from Sigma-Aldrich. RuCl₃·3H₂O was purchased from Fluorochem. FTO substrates (7 Ω/sq) were purchased from Sigma-Aldrich and cut into slides. Glacial acetic acid, pyridine, and N,N-dimethylformamide (DMF) (99.9%) were purchased from VWR. 2,2'-bipyridine-5,5'-dicarboxylic acid (dcbpy) was synthesized from 5,5'-dimethyl-2,2'-bipyridine using a modified procedure.^[25] Ru(tpy)Cl₃,^[26] and bulk UiO67^[27] were synthesized using previously published procedures.

[Ru(tpy)(dcbpy)Cl]Cl—With modifications to a reported procedure,^[12b, 14e] a flask was charged with Ru(tpy)Cl₃ (441 mg, 1 mmol), dcbpy (229 mg, 0.94 mmol), and LiCl (424 mg, 10 mmol). The contents were dissolved in 40 mL 5:1 MeOH/H₂O, and 0.75 mL of 4-ethylmorpholine was added. The mixture was refluxed under Ar for 3 h. The solvent was evaporated under reduced pressure, and the resulting solid was dry-loaded onto a silica column. The pure product eluted as the first purple band with acetone/MeOH/ sat. LiCl_(aq) 3:1:1. The solvent was reduced, and conc. HCl was added to precipitate the dark purple

solid, which was filter and washed with cold 1M HCl (91.9 mg, yield = 14%). ^1H NMR (400 MHz, DMSO- d_6) δ ppm: 7.37 (t, $J=6.59$ Hz, 2 H) 7.65 (s, 1 H) 7.72 (d, $J=5.13$ Hz, 2 H) 8.01 (t, $J=7.78$ Hz, 2 H) 8.14 (d, $J=10.25$ Hz, 1 H) 8.30 (t, $J=8.06$ Hz, 1 H) 8.74 (d, $J=7.69$ Hz, 3 H) 8.83 - 8.93 (m, 3 H) 9.11 (d, $J=8.42$ Hz, 1 H) 10.63 (s, 1 H). ESI-MS(+) (MeOH): $[\text{M}-\text{Cl}]^+$, $m/z = 614.07$ (calc. $m/z = 614.0$).

[Ru(tpy)(dcbpy)OH₂](ClO₄)₂ [1]—With modifications to a reported procedure,^[14e] a flask was charged with [Ru(tpy)(dcbpy)Cl]Cl (107 mg, 0.164 mmol), and AgClO₄ (212 mg, 1.02 mmol) to which 30 mL of H₂O/Acetone 2:1 were added. The mixture was refluxed under Ar overnight. The reaction mixture was cooled to room temperature, filtered through celite, and concentrated under reduced pressure. HClO₄ (1M, 5 mL) was added, and a violet precipitate formed, which was filtered and washed with cold 1M HClO₄ (84.6 mg, yield = 65%). ^1H NMR (400 MHz, Acetone- d_6) δ ppm: 7.46 (t, $J=6.41$ Hz, 2 H) 7.89 - 7.91 (m, 1 H) 8.05 (d, $J=5.49$ Hz, 2 H) 8.09 (td, $J=7.78$, 1.28 Hz, 2 H) 8.23 (dd, $J=8.42$, 1.83 Hz, 1 H) 8.43 (t, $J=8.06$ Hz, 1 H) 8.72 (d, $J=8.06$ Hz, 2 H) 8.82 (d, $J=8.42$ Hz, 1 H) 8.86 (dd, $J=8.42$, 1.83 Hz, 1 H) 8.90 (d, $J=8.42$ Hz, 2 H) 9.14 (d, $J=8.42$ Hz, 1 H) 10.26 (s, 1 H). ESI-MS(+) (H₂O): $[\text{M}-2\text{ClO}_4-\text{H}]^+$, $m/z = 596.04$ (calc. $m/z = 596.1$).

UiO67@FTO Thin Films—FTO slides were cleaned by sonication successively in solutions of Alconox, ethanol, and acetone. Cleaned FTO slides were immersed in a solution of 6.6 M bpdc in DMF with 30 μL of pyridine overnight to form a self-assembled monolayer (SAM). A solution of ZrCl₄ (35 mg, 0.15 mmol) and 258 μL of glacial acetic acid in 8 mL of DMF was prepared in a 22 mL vial with a rubber-lined cap and placed in an oven at 80°C for 2 h. The vials were allowed to cool, and bpdc (24.2 mg, 0.1 mmol) was added. After sonication for 10 min. one slide of SAM pre-treated FTO was placed in each vial. After incubation at 120°C for 24 h, the films were washed with DMF and incubated at room temperature in DMF overnight, followed by incubation in acetone. The final UiO67@FTO thin films (1 cm²) were dried under vacuum for further use.

UiO67-[RuOH₂]@FTO Thin Films via PSE—Complex [1] was incorporated into UiO67@FTO thin films via post-synthetic exchange (PSE) by placing one UiO67@FTO film into a vial containing 3 mL of a 1 mM solution of [1] in H₂O/acetone 3:1 for 3 days. The films were removed, washed with H₂O/acetone and incubated in H₂O/acetone for 24 h. After a further incubation in acetone overnight the UiO67-[RuOH₂]@FTO films were dried under vacuum. Nafion-coated films were made by dropping 30 μL of a Nafion solution (10 wt. % diluted 1:20 with EtOH) onto the films, which were then air-dried overnight.

Physical Measurements

^1H -NMR spectra were measured using a JEOL 400 MHz spectrometer at 293 K. The chemical shifts given in ppm are internally referenced to the residual solvent signal. HPLC-MS data were obtained using a Dionex UltiMate 3000 system on a Phenomenex Gemini C18 column (150 x 3.0 mm, 5 μm) coupled to a Thermo LCQ Deca XP Max with electrospray ionization. Solvents used for HPLC: 0.05% HCO₂H in H₂O and 0.05% HCO₂H in CH₃CN. Electronic absorption spectra were measured using a Varian Cary 50 UV-Vis

spectrophotometer. The UiO67-[RuOH₂]-@FTO films were digested in 5 mL of conc. HNO₃ for ICP-MS analysis.

Powder X-ray Diffraction

Powder X-ray diffraction patterns (PXRD) were obtained using a Simons D5000 Diffractometer (Cu K α , λ = 0.15418 nm) at 45 kV and 40 mA, using a step size of 0.02°.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) images were obtained using a Zeiss 1550 Schottky field-emission scanning electron microscope equipped with an InLens detector at 5kV acceleration voltage. MOF thin film samples were anchored to conductive carbon tape on a sample holder disk and coated using a Pd-Ir-sputter coater for 30 s.

Electrochemistry

Cyclic voltammetry (CV) was performed using a one-compartment, three-electrode configuration connected to an Autolab PGSTAT100 potentiostat controlled with GPES 4.9 software (EcoChemie). The electrode setup included an auxiliary glassy carbon disc (0.071 cm²) working electrode, which was used to monitor the solution between scans of UiO67@FTO and UiO67-[RuOH₂]-@FTO thin films, a platinum rod counter electrode, and a Ag/AgCl aqueous reference electrode (sat. KCl_(aq), 0.198 V vs. NHE). UiO67@FTO and UiO67-[RuOH₂]-@FTO thin films were measured in aqueous solutions as the working electrode, using either 0.1M KCl_(aq), 0.1M borate buffer, or 1M KNO₃ (titrated with 1M HNO₃ to reach the desired pH = 6.2 - 2.7) as a supporting electrolyte. Tafel data was collected by recording iR compensated linear sweep voltammograms (LSV) and plotting log(*j*) vs. overpotential, η . After obtaining stable CVs, a LSV was taken at 1 mVs⁻¹ in a stirred solution of 1M KNO₃ (1M ionic strength; titrated with 1M HNO₃ to reach the desired pH = 6.2 and 2.7) to prevent limiting mass transport and double layer effects. The potential was held at 1.2 V for 90s at the beginning of the experiment, followed by scanning the potential from 1.2V to 1.75V. The overpotential was calculated by converting the potential to NHE (normal hydrogen electrode), $E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.198\text{V}$, and then applying $\eta = E(\text{NHE}) - [1.23 - (0.059\text{V} \times \text{pH})]$ to adjust for the pH.

Controlled Potential Electrolysis and O₂ Detection

A two-compartment, Teflon cell was used for controlled potential electrolysis experiments (CPE). A single compartment housed the UiO67-[RuOH₂]-@FTO thin film as a working electrode (0.46 cm²) and a Ag/AgCl reference electrode (sat. KCl_(aq), 0.198 V vs. NHE). The counter electrode was a Pt plate, separated from the working and reference electrodes by a Nafion membrane. A Unisense OX-NP O₂ Microsensor connected to a Microsensor Multimeter amplifier was inserted through a septum to monitor in real time the dissolved O₂ level, and a two point calibration was used to obtain the concentration of dissolved O₂ in $\mu\text{mol L}^{-1}$. The total volume of the solution in the working compartment of the cell was 4.9 mL.

Results and Discussion

Synthesis and Characterization

Applying solvothermal conditions to FTO slides treated with bpdc to form a self-assembled monolayer (SAM)⁴¹ resulted in the growth of crystalline UiO67 films on FTO (UiO67@FTO). The films were characterized by PXRD and SEM (Figure 1), which show the deposition of crystalline UiO67 particles 500 nm in length in films with a thickness of 2 μm (Figure S1[†]).

The diffraction pattern of the films grown on FTO closely matches that of UiO67 bulk micro-crystalline powder (Figure 1a) and confirms the formation of the UiO67@FTO thin films. The water oxidation catalyst, $[\text{Ru}(\text{tpy})(\text{dcbpy})\text{OH}_2](\text{ClO}_4)_2$ ($\text{tpy} = 2,2':6',2''$ -terpyridine, $\text{dcbpy} = 2,2'$ -bipyridine-5,5'-dicarboxylic acid) [**1**], functionalized with carboxylic acid groups on bipyridine was incorporated into the UiO67@FTO thin films under mild conditions using post-synthetic exchange (PSE). Incubating UiO67@FTO in solutions of [**1**] yielded purple-colored films (UiO67- $[\text{RuOH}_2]$ @FTO) after several washings. The exchange of complex [**1**] into the UiO67 framework was confirmed by UV-Vis spectroscopy of the films, which shows the corresponding MLCT band for [**1**] at 520 nm, thus shifted ~ 20 nm when compared to [**1**] in solution (Figure 2a). The supernatant liquid from a linker exchange experiment of [**1**] with bulk UiO67 powder was examined by ^1H NMR spectroscopy. Peaks corresponding to bpdc were observed, indicating that [**1**] was incorporated into the UiO67 framework by replacement of bpdc linkers (Figure S2[†]). When the PSE was repeated under the same conditions using the non-carboxylated version of [**1**], $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$, release of bpdc into the solution was not observed (Figure S3[†]).

In fact, non-carboxylated $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ is not incorporated in the UiO-67 at all (see ESI pp. S12[†]), proving that incorporation by simple trapping is not viable. These experiments confirm that [**1**] is incorporated in the framework via a Zr-carboxylate coordination bond, rather than simply encapsulated inside the pores of the UiO67 framework. The crystallinity of the UiO67 thin film was unaltered by the PSE process, as seen from the PXRD patterns before and after the PSE (Figure 2b). The content of [**1**] in the UiO67- $[\text{RuOH}_2]$ @FTO could be determined from ICP analysis, which exhibits a ratio of Zr:Ru of 0.57:7.99 (w/w). This corresponds to 0.386 mol [**1**] per unit cell of UiO67 ($\text{Zr}_6\text{O}_6(\text{OH})_4(\text{bpdc})_{6-x}\{[\text{Ru}(\text{tpy})(\text{dcbpy})\text{OH}_2](\text{ClO}_4)_2\}_x$, $x = 0.386$), and establishes that 6.43 % of the bpdc linkers were exchanged for [**1**] during the PSE process (see ESI[†]). Furthermore, the total Zr content of the film (7.99 $\mu\text{g/mL}$) and the geometric surface area (1 cm^2) were used to determine the total surface concentration of UiO67- $[\text{RuOH}_2]$ on FTO as $2.82 \times 10^{-8} \text{ mol cm}^{-2}$. If we consider a simple monolayer of [**1**] molecules adsorbed on FTO, each with a projected area of $7.07 \times 10^{-15} \text{ cm}^2$ (per molecule), a 1 cm^2 film of adsorbed [**1**] would have a surface concentration of $2.35 \times 10^{-10} \text{ mol cm}^{-2}$ (see ESI[†]). Thus by incorporating [**1**] into UiO67@FTO thin films, the areal surface concentration of the catalyst has increased by ~ 2 orders of magnitude. This highlights the effect of the porous 3D structure of UiO67 on dramatically increasing the relative surface concentration of molecular catalysts when employed in MOF thin films.

Electrochemical Properties

Cyclic voltammograms (CVs) of UiO67-[RuOH₂]-FTO films were recorded in aqueous solution using 0.1 M KCl (pH = 6.2) as a supporting electrolyte (Figure 3). Upon scanning the anodic region, the reversible metal-centered Ru^{III/II} couple is clearly observed at 0.81 V vs. Ag/AgCl, confirming that [1] retains its molecular character, while incorporated in the UiO67 thin films. The peak separation for this redox couple is 235 mV, which is large compared to [1] in solution ($E_p = 135$ mV). The large peak-to-peak separation and peak broadening observed in the film is indicative of slow electron transfer kinetics and reflects the inherent resistance and low (or non-) conductive nature of UiO-type MOFs.⁴¹ During the first several scans, the current rapidly decreases and then stabilizes showing identical, overlapping CVs (Figure 3a). The rapid initial decrease in current is most likely a result of partial detachment of loosely bound particles from the surface of the film. SEM images of the films taken after CV measurement show larger (~ 1 μ m) particles sparsely distributed on top of a film of smaller (~ 500 nm) strongly adhered UiO67 crystallites (Figure S5†). It is important to note that no faradaic process could be observed when the solution was probed with an auxiliary glassy carbon electrode between scans (Figure S6†). This confirms that despite the detachment of a few particles, the UiO67-[RuOH₂]-FTO films are heterogeneous in nature and no leaching of [1] into the solution occurs during the experiment. To improve the stability of the films, a Nafion solution was applied to the as prepared UiO67-[RuOH₂]-FTO films. CVs of these Nafion-coated films (Figure 3b) at the same pH show considerably more stable anodic and cathodic peak currents for the Ru^{III/II} couple over multiple scans, consistent with reduced physical detachment of the particles. When measured at different pH values, $E_{1/2}$ of the first oxidation displays a pH dependence of 40 mV per decade (Figure S7†). The analogous homogenous complex that lacks the carboxylate groups shows a slope of ~59 mV per decade pH, attributed to a $1e^-/1H^+$ PCET process.^{35, 42} It is important to note that no wave for the Ru^{II/III} oxidation could be observed in SAM-coated FTO slides treated under identical conditions as UiO67@FTO during the PSE (Figure S8†). It is thus clear that [1] is not simply adsorbed to FTO, but that it has been incorporated into the UiO67 framework on UiO67@FTO thin films during the PSE.

CVs at various scan rates of UiO67-[RuOH₂]-FTO are shown in Figure 4. The Ru^{III/II} couple displays diffusion limited current, as evidenced by the square root dependence of the anodic peak current ($i_{pa} \propto \nu^{1/2}$). Diffusion-limited behavior was confirmed from the slope of a plot of $\log(i_{pa})$ vs. $\log(\nu)$, which approaches 0.5 if i_{pa} varies with $\nu^{1/2}$ (Figure S9†). Several previous reports have found diffusion-limited redox couples for transition metal complexes immobilized in MOFs^{28, 43} or related COFs (covalent-organic frameworks).⁴⁴ This has been attributed to the diffusion of counterbalancing charges within the MOF, either in the form of electrons via a redox hopping mechanism⁴³ or diffusion of supporting electrolyte within the pores of the MOF.³⁰

Controlled-potential electrolysis (CPE) experiments were performed to determine the electroactive surface concentration (Γ). After estimating the double layer capacitance ($C_d = 5.138 \mu$ F) derived from CVs taken in a potential window where there are no faradic processes present (~0.1V) (Figure S10a†), the electroactive surface concentration ($\Gamma =$

$1.08 \times 10^{-9} \text{ mol cm}^{-2}$) was calculated from the charge passed during a potential step from 0V to 1.2V (Figure S10b†).^{45, 46} This means that 3.82% of the Ru centers of [1] incorporated in UiO67-[RuOH₂]₂@FTO are electrochemically addressable. Given the low percentage of electrochemically active Ru^{II}, it is likely that the observed current arises from the oxidation of isolated Ru^{II} centers in the film nearest to the FTO electrode surface. The intermolecular distance between molecules of [1] in the MOF thin film is therefore expected to be too large for the diffusion-limited current seen in the CVs to occur via an electron-hopping mechanism. As a result, we expect the diffusion of electrolyte within the MOF thin film to be limiting in the case of UiO67-[RuOH₂]₂@FTO (*vide infra*). From the slope of the i_{pa} vs. $v^{1/2}$ plot (Figure 4b) the diffusion coefficient can be calculated according to the Randles–Sevcik equation (1),

$$i_{pa} = 0.4463nFA_2DC\left(\frac{nFvD}{RT}\right)^{\frac{1}{2}} \quad (1)$$

where i_{pa} is the anodic current maximum, n is the number of electrons transferred, A is the surface area of the electrode (1 cm^2), F is Faraday constant, C is the concentration of the redox species, v is the scan rate, R is the universal gas constant, T is the temperature, and D is the diffusion coefficient. C is the concentration of the electroactive species, which is considered to be the total amount of [1] in the UiO67-[RuOH₂]₂@FTO film (assuming an equal distribution of [1] throughout the film), divided by the total volume of the UiO67 particles that constitute the film (for more details see ESI†). Applying equation (1), a value of $D = 9.56 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ was obtained. Although this value is considerably smaller than that of the corresponding homogenous complex (Figure S11†) as well as other Ru-polypyridyl complexes in solution ($\sim 3 \times 10^{-6} - 6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$),^{47, 48} it is 2-3 orders of magnitude larger than diffusion coefficients reported for related charge transfer limited diffusional processes in other MOF systems ($\sim 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ to $10^{-14} \text{ cm}^2 \text{ s}^{-1}$).^{28, 43} One contributing factor for this difference may be the size of the electrolyte ions which were considerably more bulky (TBAPF₆, LiClO₄) in the literature reports^{28, 43} compared to the KCl electrolyte employed herein.

OER by UiO67-[RuOH₂]₂@FTO

The ability of UiO67-[RuOH₂]₂@FTO to function as an electrochemical water oxidation catalyst was examined by CVs at various pH values. Anodic scans at pH = 8.4 show current enhancements after 1.1V compared to the parent UiO67@FTO films without [1], consistent with electrocatalytic water oxidation at these potentials (Figure 5a). The Ru^{III/II} couple is constant and clearly visible at $E_{1/2} = 0.77 \text{ V vs. Ag/AgCl}$ in each and every single scan (inset Figure 5a), highlighting the intact molecular integrity of [1] during catalysis. Additional waves in a more anodic region (Ru^{3+/4+}) could not be observed as such higher oxidation states are most likely involved in catalytic turnover. The catalytic current is stable over multiple scans, and PXRD and SEM images confirm that the UiO67 framework remains intact after catalysis (Figure S12†). Upon decreasing the pH to 6.2, the Ru^{II/III} oxidation is shifted anodically to 0.81 V (Figure 5b). In addition, the onset potential is also shifted from 1.1 to 1.4 V, and the catalytic current approximately halves. It is clear that more basic

conditions favor higher activity and lower onset potential for this catalytic system. CVs in phosphate and carbonate buffers were recorded; however, the UiO67-[RuOH₂]⁺@FTO films are not stable under these conditions (Figure S13[†]), presumably due to the interference of the buffer with the attachment of the carboxylate groups of bpdc to FTO.

Controlled potential electrolysis (CPE) was employed to measure the Faradaic efficiency (FE) of the film during the OER. In 0.1 M borate buffer (pH = 8.4), a potential of 1.5V was applied over 1 hour, resulting in a current density of 11.5 $\mu\text{A cm}^{-2}$ (Figure S14a[†]). The O₂ evolved was measured *in-situ* over the course of the experiment, giving a FE = 82%. (Figure S14b[†]). A FE less than unity may point to partial film decomposition over the time-scale of the experiment, since this has already been observed in the CVs to a minor extent (Figure 3). However, the Ru^{III/II} couple is still present and features as a reversible wave in CVs taken after CPE (Figure S15a[†]). It is thus clear that [1] maintains its molecular integrity even over the course of hours under turnover conditions at applied voltages of 1.5V. SEM images taken after CPE also show UiO67 particles adhered to FTO (Figure S15b[†]).

Catalytic Tafel Behavior

Tafel data was collected at two different pH values (pH = 6.2 and 2.7) using Nafion-coated films which exhibit higher stability. A higher ionic strength supporting electrolyte (1M KNO₃) was used to avoid mass transport and double layer effects. First, CVs were recorded until obtaining stable, overlapping scans. A Tafel slope for this system was calculated based on the linear sweep voltammograms (LSV) in Figure 6a. By plotting $\log(j)$ vs. overpotential and fitting the linear portion of the curve, a Tafel slope = 166 mV decade⁻¹ was obtained under near-neutral conditions, pH 6.2 (Figure 6b). This shows better activity compared to pH 2.7 where the slope is 175 mV decade⁻¹. Such relatively large Tafel slopes are common to MOF based electrocatalysts^{24, 30, 32, 44} and is likely the result of sluggish charge transport⁴⁹ through the microporous structure of the MOF thin film. These results are in good agreement with the comparatively small diffusion coefficient obtained for this system.

Conclusions

The solvothermal growth of UiO67 on FTO resulted in thin films, which were ideal platforms in which to immobilize a well-known water oxidation catalyst via PSE. The resulting UiO67-[RuOH₂]⁺@FTO thin films were fully characterized by PXRD, SEM, UV-Vis, and ICP, showing the molecular catalyst was incorporated by exchanging 6.43 % of the linkers and the integrity of the MOF film was retained during the PSE. By doing so, the areal concentration of the catalyst in the film was increased by two orders of magnitude compared to a theoretical monolayer of [1] adsorbed on FTO.

UiO67-[RuOH₂]⁺@FTO films displayed diffusion-controlled electrochemical processes. By determining the diffusion coefficient, this behaviour was determined not to be the result of an electron-hopping mechanism as previously reported for related systems, but a direct consequence of the diffusion of the electrolyte to counter-balance charge within the MOF thin film. Examining the effect of diffusion based charge transport on catalysis in MOFs is currently ongoing in our group.

The catalytic ability of the MOF-based thin films was assessed by electrochemical techniques. The oxidation of [1] and subsequent catalysis in UiO67-[RuOH₂]₂@FTO showed a clear dependence on pH, where increasing the pH lowered the onset potential and increased the catalytic water oxidation activity. A Faradaic efficiency of 82% was obtained during CPE at 1.5V, and the Tafel behavior was evaluated giving a slope of 166 mV decade⁻¹. When considering the activity, it is important to note that the low conductivity of the UiO67 framework inhibits charge transport through the film and conspires to low current densities. Improvements to the charge-transport properties of such MOF films will certainly be necessary for future, more efficient catalytic systems, which is the focus of ongoing work.

While the observed current densities are a drawback, this first principle approach successfully demonstrates that a molecular complex can be electrochemically addressed and fully characterized inside a MOF thin film, while functioning as a water oxidation catalyst. Examining the films after catalysis, the molecular nature of the Ru(II) complex incorporated into the MOF thin films is retained, as evidenced by the presence of the reversible Ru^{III/II} couple before and after catalysis.

Reported here is one of the first examples of a molecular catalyst incorporated into a MOF thin film for electrocatalytic water oxidation.³⁹ This initial work is a step forward to using the tunability, selectivity, and high activity of molecular electrocatalysts in combination with the high porosity, but well-defined structure of MOFs with the goal of creating heterogeneous devices for catalytic processes relevant to renewable energy and artificial photosynthesis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

Financial support from the Swedish Research Council, The Swedish Energy Agency, and the Knut and Alice Wallenberg Foundation is gratefully acknowledged. The authors would like to thank Prof. Dr. Haining Tian for assistance with the O₂ detection experiments, Dr. Jean Pettersson for the ICP-MS measurements, and Dr. Hemlata Agarwala for helpful discussions.

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Figure 1.

a) PXRD of UiO67@FTO films (red), UiO67 as a bulk microcrystalline powder (black), and bare FTO (blue). b) SEM image of UiO67@FTO film.

Figure 2.

a) UV-Vis spectra of UiO67-[RuOH₂]₂@FTO films (after PSE) (red), UiO67@FTO (before PSE) (black-dotted), and [1] in solution phase with H₂O as the solvent (black-solid). The arrows indicate the MLCT band of [1]. b) PXRD of films before (red) and after (blue) PSE compared with bare FTO (black).

Figure 3.

a) CVs of UiO67-[RuOH₂]@FTO in 0.1 M KCl (pH = 6.2) at a scan rate $\nu = 100 \text{ mV s}^{-1}$, showing initial scans of the Ru^{III/II} couple. b) CVs (first 20 scans) of Nafion-coated UiO67-[RuOH₂-]@FTO in 1 M KNO₃ (pH = 6.2).

Figure 4.

a) CVs of UiO67-[RuOH₂]⁺@FTO at scan rates from 10 mV s⁻¹ to 200 mV s⁻¹ in 0.1 M KCl (pH = 6.2). b) plot of *i*_{pa} vs. *v*^{1/2} (black) and *i*_{pa} vs. *v* (blue), showing a linear dependence of *i*_{pa} on *v*^{1/2}, which indicates a diffusion controlled process.

Figure 5.

CVs of UiO67-[RuOH₂]₂@FTO at a) pH = 8.4 and b) pH = 6.2, showing a catalytic wave following the Ru^{3+/2+} oxidation. Insets show region of the Ru^{III/II} couple, confirming the integrity of the molecular species in the UiO67-[RuOH₂]₂@FTO thin films during catalysis.

Figure 6.

a) LSVs of Nafion-coated UiO67-[RuOH₂]@FTO in 1M ionic strength supporting electrolyte (pH = 6.2 and 2.7; 1M KNO₃) at a scan rate $\nu = 1 \text{ mV s}^{-1}$ with iR compensation, and b) corresponding Tafel plots of UiO67-[RuOH₂]@FTO.

Scheme 1.

Schematic representation of UiO67-[RuOH₂]@FTO thin films⁴⁰ and the structure of [Ru(tpy)(dcbpy)OH₂]²⁺.