Light assisted solar fuel production by artificial CO_2 Reduction and water Oxidation

Deliverable D2.4

Anodes for WOC

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EXECUTIVE SUMMARY

This public report, Anodes for WOC, is a deliverable of the LICROX Project which is funded by the European Union’s H2020 Programme under Grant Agreement No. 951843 and contains information about molecular Cu complexes containing tetraamide macrocyclic ligands functionalized with thiophene groups (H_4Mac-Thio) that can be polymerized on conductive surfaces. Given the confidential nature of the work developed, here we will describe only the redox and catalytic properties of the Cu complex, more details more details are to be found in the confidential final review report. The best hybrid molecular material for WO catalysis described here will be later on polymerized into $BiVO_4$ semiconductor materials in order to achieve light induced water oxidations catalysis. Ultimately the best molecular photoanodes will be integrated into a PEC for the generation of solar fuels.

Contents

WP2. CO2R tandem catalysis and WOC

The role of WP2 is to implement the preparation of efficient catalysts that will perform the chemical reaction associated with the CO_2 reduction reaction (CO2RR) to yield solar fuels and in combination with the WOC to give oxygen gas in order to achieve high catalytic rates (high currents) and low working voltages.

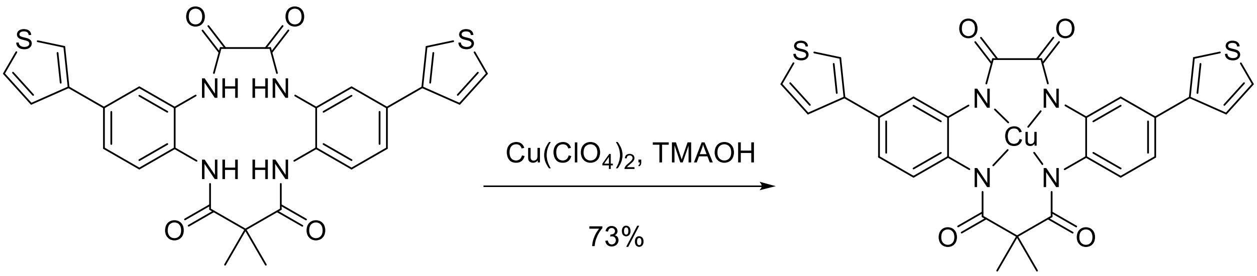
1. Purpose of “Anodes for WOC” (D2.4)

LICROX’s final goal is the fabrication of a compact photoelectrochemical Cell (PEC) device for the production of reduced carbon products of 1 or 2 carbon atoms from CO_2, such as ethylene or ethanol. This kind of devices drive water oxidation and CO_2 reduction using sunlight as the only external energy source. The photoanode of such device will have to efficiently trap photons and carry out water oxidation. The later process needs the aid of a water oxidation catalyst (WOC). Ideally, this WOC should be made of abundant, nontoxic and cheap elements, like Fe or Cu, and achieve dark currents in the range of 20-30 mA/cm^2 in H_2O at pH values close to neutrality with an applied bias in the range of E = 1.5-1.7 V *vs*. RHE.

The WOC described in this deliverable is electropolymerized into carbon-based surfaces, namely glassy carbon disk electrodes (GC_d), carbon paper (C_p) and carbon felt (C_f). Recently the Llobet group at ICIQ reported the electropolymerization of a Ru WOC using thiophene monomers, on carbon based electrodes.[1] Here, we report a parallel strategy but using a new Cu WOC with a tetra-amido macrocyclic type of ligand (TAML) containing thiophene groups,[2] **$[Cu^{II}(Mac\text{-}Thio)]^{2-}$**. The complex is then electropolymerized on the surface of the graphitic electrode through consecutive CV cycles. The electrochemical performance of this new hybrid materials with regard to their capacity to carry out the electrocatalytic water oxidation reaction is then tested at neutral pH in a phosphate buffer aqueous solution, reaching catalytic currents over 31 mA/cm^2 at applied potential of 1.7 V *vs*. RHE.

2. Synthesis of the H_4Mac-Thio ligand and its Cu(II) complex

Scheme 1 shows the synthetic procedure for the preparation of the **$[Cu^{II}(Mac\text{-}Thio)]^{2-}$** complex using the free ligand H_4Mac-Thio and $Cu(ClO_4)_2$ as starting materials. Figure 1 shows the ^{1}H-NMR spectrum of H_4Mac-Thio free ligand recorded in d_6-dmso at room temperature, whereas Figure 2 shows the 2D ^{1}H-^{13}C-NMR spectra. The signals integrate for a total of 22 protons, which is in accordance with the proposed structure for H_4Mac-Thio. The shifts for the signals assigned to $^1H_5$ and $^1H_3$ are split 0.25 ppm in both cases. Moreover, 2D HSQC ^{1}H-^{13}C spectra shows clearly that the signals at 7.42 and 7.66 ppm (assigned to $^1H_5$) correlate for the same ^{13}C nuclei at 127.1 ppm. The same is true for signals at 7.68 and 7.92 ppm (assigned to $^1H_3$), which correlate to the ^{13}C nuclei at 123.4 ppm. We can ascribe this phenomenon to different isomers around the thiophen-2-yl moiety.



Scheme 1. Synthetic procedure for preparation of the **$[\mathrm{Cu^{II}(Mac\text{-}Thio)}]^{2-}$** *complex .*

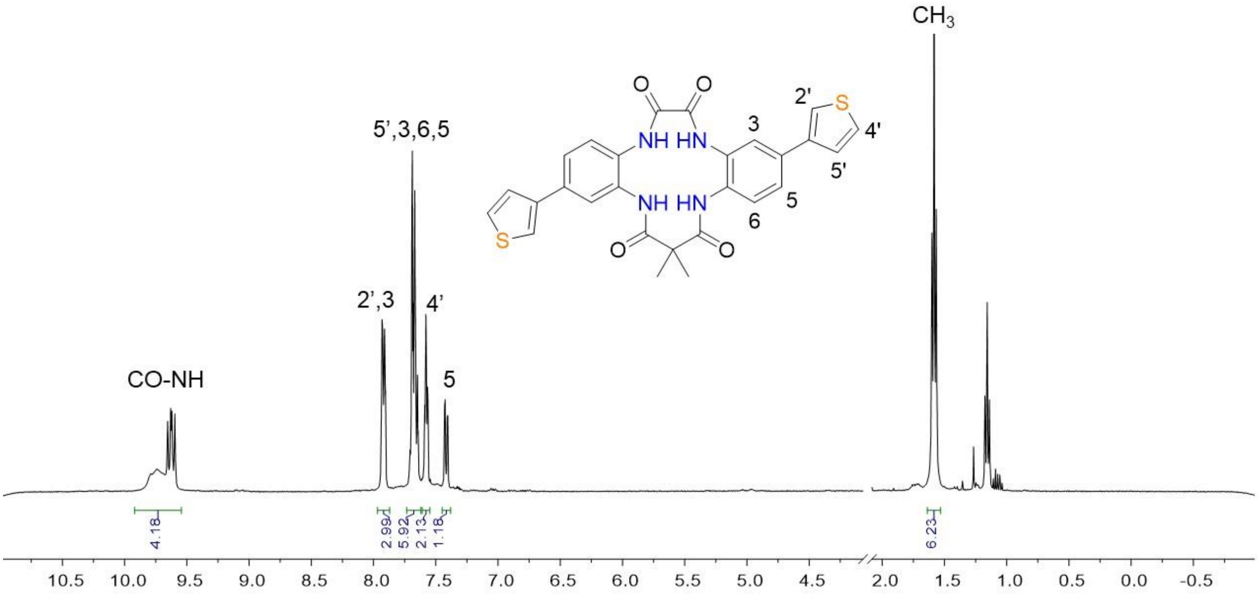


Figure 1. ^{1}H-NMR spectrum of H_4Mac-Thio in d_6-dmso with proton assignment.

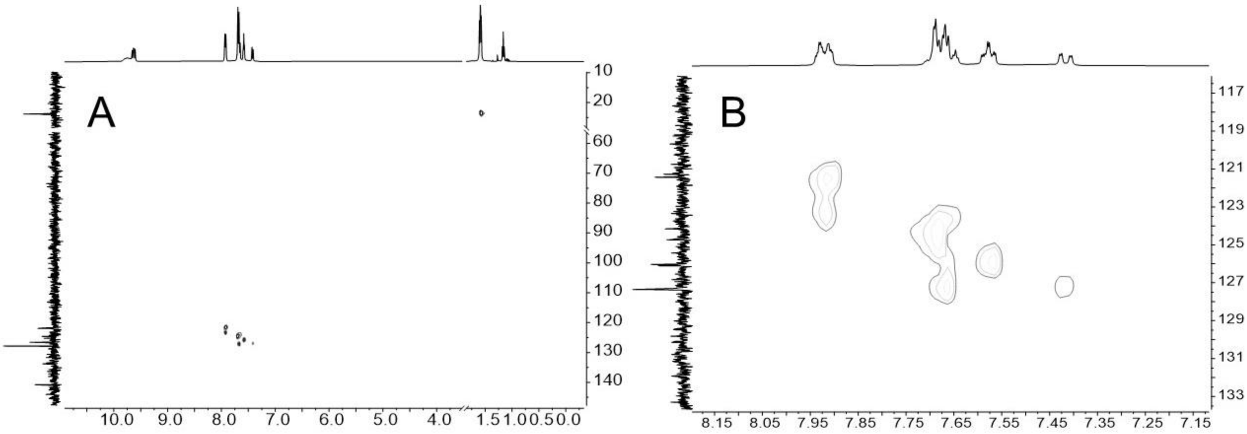


Figure 2. A) 2D HSQC ^1H-^{13}C NMR spectra of H_4Mac-Thio in d_6-dmso. B) Enlargement of the aromatic region.

3. Anchoring $[Cu(Mac\text{-}Thio)]^{2-}$ and its performance as a water oxidation catalyst.

The electrochemical properties of **$[Cu^{II}(Mac\text{-}Thio)]^{2-}$** have been studied in acetonitrile by means of cyclic voltammetry (Figure 3A). The anodic wave at 0.3V vs. NHE is assigned to the Cu^{II} to Cu^{III} oxidation process, and is in agreement with previously reported related Cu(II) complex without the thiophene group.[3] The relatively low oxidation potential can be ascribed to the strong σ-donating ability of the four amidate groups in the structure of the ligand.[2,4] The anodic current at roughly 1.0 V is due to the oxidation of the thiophen-2-yl moiety forming a radical species that is responsible for the electropolymerization process. The returning wave at -0.35V *vs*. NHE are due to the for the reduction of the previously oxidized Cu(III) center. Figure 3B shows the results of 50 CV cycles within the potential range -0.45V to 1.35V vs. NHE, which generates the molecular anode **poly-$[Cu^{II}(Mac\text{-}Thio)]^{2-}$@$GC_d$**, with a surface loading of $\Gamma = 62.2$ nmol/cm^2 based on the Cu complex. Figure 4 shows the CV of the **poly-$[Cu^{II}(Mac\text{-}Thio)]^{2-}$@$GC_d$** hybrid materials at different scan rates in a clean electrolyte solution of MeCN with 0.1M of NH_4TfO as supporting electrolyte.

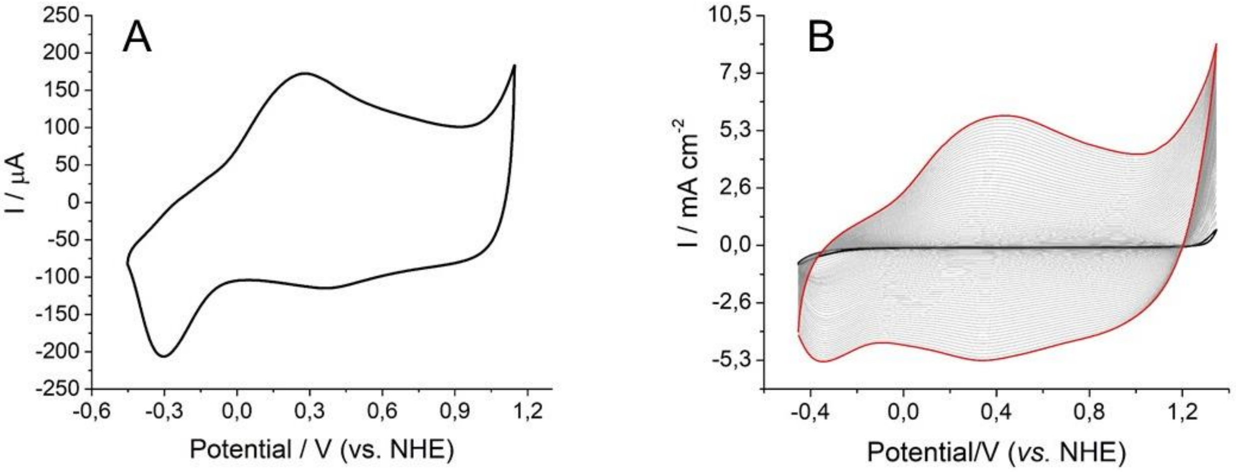


Figure 3. A) Cyclic voltammetry of ***[Cu^{II}(Mac-Thio)]$^{2-}$*** *(3 mM) in acetonitrile with 0.1M of NH_4TfO. Scan rate: 50 mV s^{-1}, using a GC_d (S=0.076 cm^{-2}) as a working electrode. B) Electropolymerization (50 cycles) of* ***[Cu^{II}(Mac-Thio)]$^{2-}$*** *(1mM) in acetonitrile using 0.1M of NH_4TfO as supporting electrolyte . Scan rate: 50 mV.s^{-1}. Black: Initial voltammogram; Red: Final Voltammogram; gray: Voltammograms between initial and final.*

We also anchored the molecular catalyst on a carbon paper (C_p) electrode. Figure 4 (left) shows 50 CV cycles of a 0.1 M solution of **[Cu^{II}(Mac-Thio)]$^{2-}$** at potentials -0.2V to 1.2V *vs*. NHE. This generates the polymerization of the Cu complex at the surface of the electrode forming for **poly-[Cu^{II}(Mac-Thio)]$^{2-}$@C$_p$**, with a surface loading of Γ = 4.14 nmol.cm^{-2}. To evaluate the performance of this new hybrid material it was submerged in clean electrolyte solution of 0.1 M aqueous phosphate buffer at pH = 7.1. A CV at a scan rate of 50 mV.s^{-1} was then carried out that is depicted in Figure 4 (right). The obtained catalytic current at 1.44 V *vs*. NHE was 22.2 mA.cm^{-2} (10.9 mA.cm^{-2} at 1.3V vs. NHE). Controlled potential electrolysis (CPE) experiments were conducted (Figure 5A) over 12 min and over 40 minutes (Figure 5B) and the amount of oxygen generated was measured using a Clark electrode. After the passage of 4.53 C/cm^2, a total of 2.25 µmol of O_2 was generated, which correspond to a faradaic efficiency of 96% and a TON ca. 2710 over 40 min. Finally, a CV of the working electrode before and after bulk electrolysis is shown in Figure 5C. As can be observed there is an increase of current at around 1.1 V after the electrolysis, which can be ascribed to some electrode oxidation that can produce the partial detachment of the polymer. After 40 minutes of electrolysis, 73% of the catalytic activity is still maintained showing a good stability of the hybrid material.

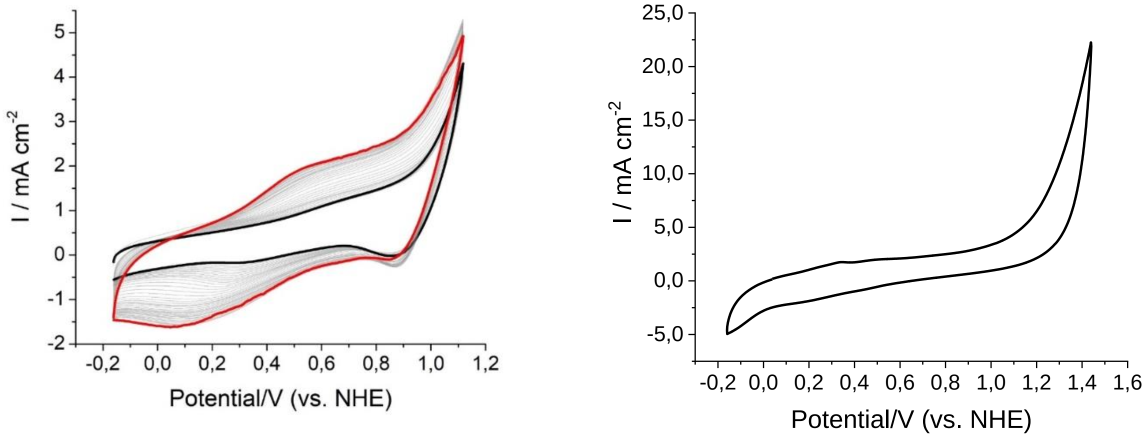


Figure 4. Left, Cyclic voltammograms of the electropolymerization process of ***[Cu^{II}(Mac-Thio)]$^{2-}$*** *(1 mM) in acetonitrile with NH_4TfO (0.1 M) using C_p as a working electrode. Scan rate: 50 mV.s^{-1}. Right, Cyclic voltammogram of poly-***[Cu^{II}(Mac-Thio)]$^{2-}$@C_p** *in a clean electrolyte solution of 0.1 M aqueous phosphate buffer at pH = 7.1.*

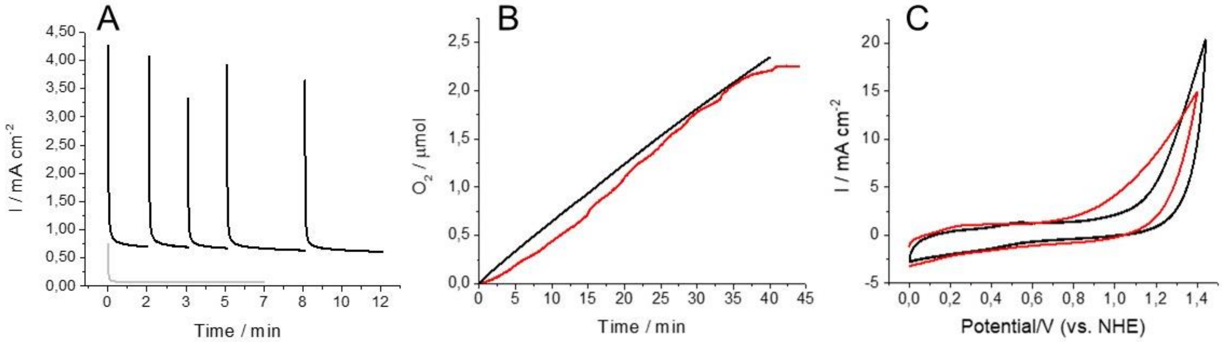


Figure 5. A) Controlled Potential Electrolysis of ***[Cu^{II}(Mac-Thio)]$^{2-}$@C_p*** *(black) and C_p (gray) at an applied potential of 1.2V vs. NHE. B) Bulk electrolysis of* ***[Cu^{II}(Mac-Thio)]$^{2-}$@C_p*** *at an applied potential of 1.2V. Red line represents the generation of O2 in µmol over time measured with a Clark electrode. Black line represents the generation of O_2 over time calculated from the amount of charge that passed through the anode. Charge: 4.56 C.cm^{-2}. Faradaic efficiency calculated as (mmol O_2 measured from Clark electrode)/ (mmol O_2 measured from the charge) was 96%. C) Cyclic voltammogram of* ***[Cu^{II}(Mac-Thio)]$^{2-}$@C_p*** *in phosphate buffer (0.1M, pH = 7.1) before (black line) and after (red line) 40 min of bulk electrolysis at an applied potential of 1.2V.*

Finally, the electropolymerization was carried out on a carbon felt (C_f) working electrode, that has a larger volume than C_p and GC_d. The results of the electropolymerization process in acetonitrile are shown in Figure 6 and give a loading of Γ= 19.1 nmol/cm^2, which is almost 5 times larger than the loaded amount over C_p. The oxidation waves are very wide but we can clearly see the redox waves associated with the Cu$^{III/II}$ couple that shows a parallel behavior to the electrochemistry observed on the GC_d and C_p electrodes. The catalytic performance of the **poly-[Cu^{II}(Mac-Thio)]$^{2-}$@C_f** was explored in clean pH 7 phosphate buffer electrolyte solution, and is shown in Figure 7. A catalytic current density of 31.3 mA/cm^2 is achieved at 1.3 V *vs.* NHE (1.7 vs. RHE) which falls within the desired values proposed in the present project. A controlled potential electrolysis over 20 min (Figure 7B) shows a stable current of 12.6 mA.cm^{-2}, which implies a TON = 1.6.10^{6}, assuming a Faradaic efficiency of 96%.

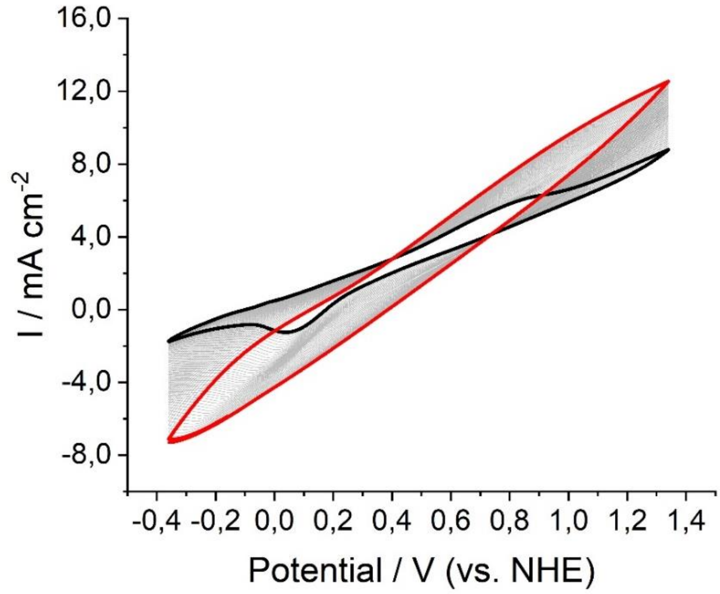


Figure 6. 50 consecutive CVs at 50 mV/s of a solution of ***[Cu^{II}(Mac-Thio)]$^{2-}$*** *(1 mM) in acetonitrile with NH_4TfO (0.1 M), using C_f as a working electrode, showing the electropolymerization process.*

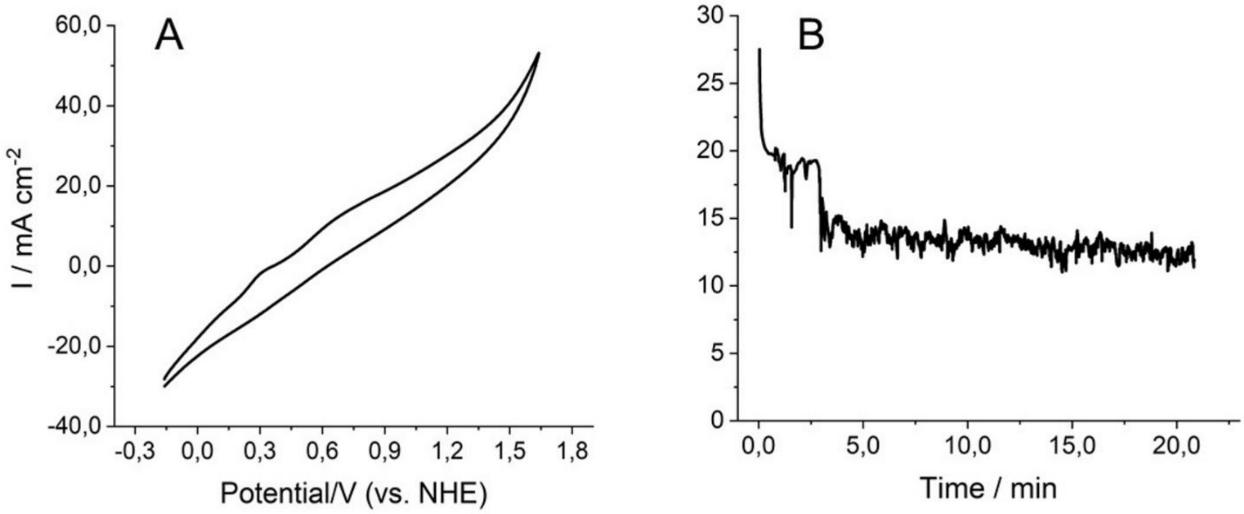


Figure 7. A, Cyclic voltammogram of ***poly-[Cu^{II}(Mac-Thio)]$^{2-}$@C_f*** *in a phosphate buffer solution (0.1M, pH = 7.1). B, Controlled Potential Electrolysis of* ***poly-[Cu^{II}(Mac-Thio)]$^{2-}$@C_f*** *at an applied potential of 1.2V vs. NHE.*

4. Conclusions and future prospects

The electropolymerization of the Cu(II) complex containing a thiophene unit, **$[Cu^{II}(Mac\text{-}Thio)]^{2-}$,** has been successfully carried out using graphitic electrodes namely: a glassy carbon disk (GCd) a Carbon paper, (C_p) and a Carbon felt (C_f). This has generated the hybrid molecular materials **poly-$[Cu^{II}(Mac\text{-}Thio)]^{2-}$@$GC_d$**, **poly-$[Cu^{II}(Mac\text{-}Thio)]^{2-}$@$C_p$** and **poly-$[Cu^{II}(Mac\text{-}Thio)]^{2-}$@$GC_f$** that behave as excellent molecular anodes for the electrocatalytic oxidation of water to dioxygen reaction. In particular, the **poly-$[Cu^{II}(Mac\text{-}Thio)]^{2-}$@$GC_f$** material achieves current densities over 30 mA/cm^2 at 1.5 V *vs*. RHE at neutral pH. Further a CPE at an E_{app} = 1.2 V *vs*. NHE (1.6 *vs*. RHE) achieves a stable current density of approx. 13 mA/cm^2 during 20 minutes that imply a TON larger than of 1.6 million.

Once we have fully characterized this highly performing molecular anodes, our next goal will involve the polymerization of the **$[Cu^{II}(Mac\text{-}Thio)]^{2-}$** monomer into semiconductive $BiVO_4$ materials and their integration into photoelectrochemical cells (PECs).

5. References

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