Electrocatalysis in confinement: metal-organic frameworks for oxygen reduction

Hoefnagel, M.E.

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Chapter 6

Summary, Conclusion and Outlook

6.1 Summary and Conclusions

Molecular electrocatalysts are interesting for catalytic reactions relevant to the energy transition due to their tuneability and the possibility to study structure-activity relationships. However, they generally yield low catalytic current densities. Embedding molecular catalysts in metal organic frameworks (MOFs) is an attractive strategy to immobilize them onto electrodes and thereby increase catalytic current densities. Due to the highly porous nature of MOFs, a large number of catalysts can be immobilized close to the electrode surface while the advantages of molecular catalysts are retained. However, the effect of embedding the catalyst in a MOF on the catalyst itself and its catalytic mechanisms is widely overlooked.

Confinement effects on the embedded catalyst are difficult to predict and can have both positive and negative outcomes on catalytic performance. Reports on molecular catalysts embedded in MOFs have shown that the limiting factor for the catalytic reaction in MOFs can be found in 1) electron transport, 2) mass transport of reactants and products, or 3) a low activity of the catalytic site itself. Challenges that remain to be investigated include optimization of electron transfer and mass transport through the MOF, stability of the MOF and the catalyst embedded in the MOF, the effect of embedment on the catalytic mechanism and the precise location in the MOF where catalysis takes place. In this thesis, some of these challenges were addressed; the effect of confinement on the catalytic performance of the catalyst was described in Chapter 2. The effect of confinement on the catalyst itself was reported in Chapter 3. Electron transfer in redox-active MOFs and the effect of those MOFs on the catalyst and its performance were studied and the results are discussed in Chapters 4 and 5. The Cu-tmpa catalyst was selected for these studies as it was previously well-characterized in homogeneous solution, enabling fair comparison. Furthermore, the catalyst is limited by a lack of long-term stability and therefore immobilization in a MOF appears an attractive strategy to improve its performance.

The experiments described in Chapter 2 were conducted to study the effect of confinement of the catalyst in a MOF on the activity, reusability and the selectivity of the ORR. Immobilization of the Cu-tmpa catalyst in the NU1000 MOF leads to high catalytic current density of -7.5 mAcm^{-2} (at 0.3 V vs. RHE with a dropcast containing 97 nmol of Cu-tmpaCOOH) and good reusability of the Cu-tmpa catalyst. Chronoamperometry (CA) for 30 hours, spread over 6 days, resulted in a stable current density, illustrating the reusability of the MOF-embedded catalyst. For comparison, a homogeneous solution of 5 µM (250 nmol) of Cu-tmpa yields −1 $mAcm^{-2}$ for 28 h of CA divided over 3 days with significant loss of current density.

The selectivity of the ORR catalyzed by the NU1000|Cu-tmpaCOOH MOF was investigated using rotating disk electrode (RDE) experiments with Koutechy-Levich analysis, with rotating ring disk electrode (RRDE) experiments and by measuring the H_2O_2 concentration in the electrolyte during CA directly with a reflectometer. These experiments unanimously showed that the ORR catalyzed by NU1000|Cu-tmpaCOOH is directed towards water as the product, while the Cu-tmpa catalyst in homogeneous solution makes 50% H_2O_2 under the same conditions. A possible explanation for formation of H_2O in the MOF is the retention of the H_2O_2 intermediate in the MOF pores in close proximity to the catalyst and therefore rapid further reduction towards water. Another possibility is the active species in NU1000|Cu-tmpaCOOH no longer being Cu-tmpa, but another species that directs the ORR to water rather than hydrogen peroxide. The nature of the true active species has been investigated and is described in more detail in Chapter 3. Scan-rate dependence studies for the $Cu^{II/I}$ redox couple yielded a trumpet-shaped Laviron plot, indicating that electron transfer is slow and may be rate limiting. Integration of the redox couple showed that only 0.23 nmol (0.24%) of the Cu centers in the MOF were activated during a CV experiment. Therefore, use of redox active MOFs was investigated to mitigate charge transport limitations, and the results are described in Chapters 4 and 5.

In Chapter 3 the effect of confinement on the molecular catalyst itself is described. It is well-known that molecular catalysts do not always remain in their homogeneous state and regularly form heterogenous deposits under (electro)catalytic conditions. Despite this well-known risk of homogeneity loss, reports on molecular catalysts embedded in MOFs have thus far not described the formation of heterogenous deposits from molecular catalysts in MOFs. This is especially important for Cu-based molecular catalysts, because of the fast kinetics of their ligand-exchange reactions, which can cause Cu atoms to be pulled from the equilibrium by formation of heterogeneous deposits.

The ex-situ and operando X-ray absorption spectroscopy (XAS) studies reported in Chapter 3 were performed to shed light on the Cu species formed in NU1000|Cu-tmpaCOOH before, during and after ORR. Linear combination fitting of the X-ray absorption near edge spectroscopy (XANES) of NU1000|Cu-tmpaCOOH with Cu^0, Cu^+ and Cu^{2+} standards reveal the expected Cu^{2+} oxidation state before the reaction. During the reaction a Cu^0 oxidation state dominates (78%), which reoxidizes to Cu^{2+} after the catalytic reaction. Extended X-ray absorption fine structure (EXAFS) showed a significant Cu-Cu contribution during the catalytic reaction, confirming formation of Cu^0 clusters. A Cu-Cu coordination number of 8.35, with radial distance of 2.55 Å and average cluster diameter of 1.3 nm were determined from fitting of the first shell of the Cu-Cu and Cu-O/N EXAFS peaks. The extent of cluster formation was found to increase with more negative potential. The electrochemical signals show clearly distinct redox couples before and after the reaction, suggesting that reoxidation of clusters does not result in regeneration of Cu-tmpa. The appearance of Cu-O or Cu-N peaks in EXAFS, similar to those found previously for CuOx, taken after the reaction suggests formation of Cu^{2+} clusters. These results emphasize the importance of applying operando spectroscopy techniques to study the homogeneity of molecular catalysts embedded in MOFs, as well as correlating those characterizations with electrochemistry. Only by combining results of surface-sensitive techniques such as cyclic voltammetry with those of bulk-sensitive techniques such as XAS thorough characterization of the chemical nature of the catalytic system can be performed.

The experiments presented in Chapter 4 are aimed at comparing the effects of embedding the molecular catalyst in a redox-active MOF in comparison to a redox-inert MOF. Catalysis in MOFs is often limited by electron transfer as the majority of MOFs consist of redox-innocent components. A series of naphthalene diimide (NDI) based MOFs was developed as a platform for catalysis, yet thus far catalysts have not been embedded in this platform. Chapter 4 compares the properties of the Cu-tmpaCOOH catalyst embedded in such an NDI MOF with those of the same catalyst in the redox-inert NU1000 MOF, which are extensively described in Chapter 2 and Chapter 3. Embedding the Cu-tmpaCOOH catalyst in the redox-active Zr-(BTD-NDI) MOF increases the percentage of addressable redoxactive moieties from 3% in NU1000|Cu-tmpaCOOH to 25% in Zr-(BTD-NDI)|Cu-tmpaCOOH. Thus, the NDI linkers successfully transport electrons to the catalyst. However, more time is required to reduce all components in the redox-active MOF as the cation migration or proton-transfer dependent NDI/NDI^{2-} two-electron reduction is kinetically more challenging than the $Cu^{II/I}$ reduction.

The effect of embedment in the Zr-(BTD-NDI) MOF on catalyst homogeneity has been investigated by XAS as described for NU1000 in Chapter 3. Both the NU1000|Cu-tmpaCOOH and Zr-(BTD-NDI)|Cu-tmpaCOOH MOFs exhibit Cu^0 cluster formation during ORR, albeit to a smaller extent of 69% in the NDI-based MOF compared to 78% in Zr-(BTD-NDI). A possible explanation for this observation may be found in the redox-active linkers, which are also capable of catalyzing the oxygen-reduction reaction, thereby preventing accumulation of electrons and overreduction of the copper sites. Furthermore, significantly less Cu^0 clusters are formed in the Zr-(BTD-NDI)|Cu-tmpaCOOH MOF under helium atmosphere compared to oxygen atmosphere. This result is attributed to the retention of the H_2O_2 intermediate in MOF pores during the ORR, leading to formation of strongly oxidizing $HO^\bullet$ species. These strongly oxidizing species may oxidize the tmpa ligand and as a result, cause formation of free Cu atoms that can more easily form clusters.

The catalytic activity and selectivity of the NU1000|Cu-tmpaCOOH and Zr-(BTD-NDI)|Cu-tmpaCOOH MOFs have been compared with cyclic voltammetry and chronoamperometry under oxygen atmosphere with a rotating disk electrode. Both MOFs show a catalytic current density of -4 mAcm^{-2}, a Tafel slope of -141 mV/dec and $FE_{H2O2} < 10\%$. To explain the almost identical catalytic performance of the two MOFs, the factors limiting the catalytic reaction should be determined. A likely candidate for the limiting factor of ORR in these MOFs is mass transport of O_2. The Zr-(BTD-NDI)|Cu-tmpaCOOH MOF has smaller pores (10 Å) than the NU1000|Cu-tmpaCOOH MOF (30 Å). Therefore, even if more electrons can reach the Cu sites in Zr-(BTD-NDI)|Cu-tmpaCOOH, diffusion of O_2 through the MOF will be slower. Thus, if O_2 transport is the rate-limiting factor, the ORR catalyzed by Zr-(BDT-DNI)|Cu-tmpaCOOH should be significantly slower than the ORR catalyzed by NU1000|Cu-tmpaCOOH. The equal Tafel slopes for these MOFs show that this is not the case, making it unlikely that mass transport through the MOF is limiting catalysis.

As reported in Chapter 2, the active site in MOF|Cu-tmpaCOOH is a very fast catalyst for the ORR, making the catalyst itself an unlikely candidate to limit the reaction. The lack of improvement of catalytic activity in a redox-active MOF compared to a redox-inert MOF may make electron transfer seem an unlikely limiting factor as well, but it cannot be ruled out. The two-electron transfer in NDI/NDI^{2-} reduction is coupled with migration of either cations or protons, making this transfer significantly slower than the single-electron transfer in the $Cu^{II/I}$ redox couple. Therefore, electron hopping between linkers may be slower than the k_{obs} of the ORR catalyzed by Cu-tmpaCOOH, making ORR activity still dependent on electron hopping between Cu centers.

In Chapter 5 are reported the charge transport mechanisms in NDI MOFs in aqueous electrolyte and the effect of pH on these mechanisms. Charge transport mechanisms in the Zr-(dcphOH-NDI)@FTO MOF thin film in organic solvents have been studied in detail previously, but not in aqueous electrolyte. The CV of Zr-(dcphOH-NDI)@FTO in DMF shows two redox waves, corresponding to the NDI/NDI$^{\bullet-}$ and NDI$^{\bullet-}$/NDI^{2-} reductions, that merge into a single redox wave in aqueous electrolyte. The waves shift anodically because of the stabilization of negative charge by water and the higher local cation concentration in the MOF.

Pourbaix diagrams, spectroelectrochemistry measurements and differential pulse voltammetry reveal two different electron transfer mechanisms leading to formation of two distinct species depending on pH. The Pourbaix diagram shows two linear regions separated by a drop in potential: a slope of 4 mV/dec is found at pH ≥ 3.5 and a slope of 59 mV/dec at pH ≤ 3. The two regions are separated at a pH value that coincides with the pKa of the MOF node, indicating that the nature of the species that is formed upon reduction of the NDI linker depends on the presence of a hydrogen bonding network in the MOF pore. At pH ≥ 4 the two-electron reduction of NDI proceeds via two separate electron transfer (ET) steps and at pH ≤ 3 the reduction of NDI proceeds via two proton coupled electron transfer (PCET) steps. In the latter case, the second PCET step follows upon a protonation in the first step and is therefore thermodynamically more favorable. Differential pulse voltammetry shows that only one species is formed at pH 2, while a mixture of the protonated and the deprotonated species are formed in pH 3-4.

Scan-rate dependence studies revealed that reduction of the NDI linker is kinetically more facile at low pH compared to high pH, most likely due to protonation in the MOF pore environment. In contrast, apparent diffusion-coefficient (D_e^{app}) values describing electron-hopping rates through the MOF film are not influenced by electrolyte pH. Thus, with cyclic voltammetry at short timescales an effect is observed of pH on the kinetics of electron transfer, while with chronoamperometry at larger time scales no effect of pH is found on charge transport throughout the framework. A possible explanation for these observations is rapid depletion of protons available in the MOF upon the reduction of the first linkers by proton-coupled electron transfer. This leads to a local increase of the pH and a change in electron transfer mechanism. The reduction of the MOF film at larger timescales has to proceed by electron transfer coupled to migration of electrolyte cations, making the electron-transfer rate dependent on cation-diffusion coefficients, and independent of pH.

6.2 Outlook

In Chapter 1 a number of challenges are identified to be investigated when embedding a molecular electrocatalyst in a MOF. Some of these challenges were attended to and are discussed in this thesis, as summarized in Section 6.1, and some remain to be addressed. These challenges can be roughly assigned to electron transport to the molecular catalyst, mass transport through the MOF to the catalyst and from the bulk electrolyte to the electrode surface, or the effect of the MOF on the molecular catalyst structure.

The results reported in Chapters 3 and 4 show the formation of Cu^0 clusters under operando conditions in NU1000|Cu-tmpaCOOH and Zr-(BTD-NDI)|Cu-tmpaCOOH dropcasted onto an electrode. However, it is not clear from the electrocatalytic and XAS experiments at which exact location in the MOF these clusters form. Furthermore, it is still unclear whether catalysis takes place primarily at the Cu^0 clusters or at the remaining Cu-tmpaCOOH catalysts in the MOFs. As reported in Chapter 2 and 3, cyclic voltammetry, a surface-sensitive technique, shows nearly full conversion to Cu^0 clusters while XANES, a bulk-sensitive technique, reports a lower fraction of 78% cluster formation. Therefore, it is likely that cluster formation happens mostly to catalysts close to the electrode surface, where electrons are injected first.

Electron-transfer efficiency studies described in Chapter 4 show that 3−25% of redox-active moieties can be addressed electrochemically. It is likely that these moieties are close to the electrode. However, investigation by 3D mapping could give more direct evidence on the location of the Cu^0 clusters. Spatial mapping of Cu^0 cluster formation could be done by 3D scanning transmission X-ray microscopy (STXM) of the Cu K-edge. The group of Weckhuyzen reported this technique for nanoscale chemical imaging of aluminum in zeolite materials.[1] The technique allows for the visualization of spatial distribution of the amount as well as the coordination environment of the studied metal.

Studies on electron transfer and mass transport in MOFs are usually performed in fundamental, isolated experiments in which no catalytic reaction is taking place. Furthermore, quite often these studies are performed in organic solvents. To advance catalysis in MOFs the field should move more towards investigating electron transfer and mass transport mechanisms in aqueous electrolytes and coupled to catalytic reactions. Experiments such as the previously mentioned operando STXM or operando XPS with spatial resolution could offer insight into the exact location of catalysis and nanoparticle formation, and as a result, on whether electron transfer or mass transport is limiting the rate of the reaction. When catalysis takes place close to the electrode-MOF interface, it is most likely limited by electron transfer. When catalysis takes place close to the MOF-electrolyte interface, mass transport is the more likely limiting factor.

The studies reported in Chapter 4 indicate the faster redox transition of $Cu^{II/I}$ in Cu-tmpaCOOH compared to the NDI/NDI^{2-} transition. The NDI transition is coupled to migration of cations or, at low pH, to proton transfer. The higher reversibility of the $Cu^{II/I}$ redox couple raises the question whether this transition is coupled to migration of ions when the catalyst is embedded in a MOF. Furthermore, it is not confirmed in literature that the NDI redox transitions are also coupled to migration of cations in aqueous electrolyte, as they are in organic solvents. Alternatively, the accumulating negative charge may be stabilized by water molecules. A comparative study of the apparent diffusion coefficients[3] of cations with varying radii in the Zr-(BTD-NDI) and NU1000|Cu-tmpaCOOH MOFs in aqueous electrolyte could reveal cation dependence of the NDI and Cu redox transitions, respectively.

A major challenge that did not receive much attention in this thesis is the limitation of mass transport. This can be either the transport of substrate from the bulk electrolyte towards the electrode, or the transport of substrate, protons, cations and products through the MOF framework. The transport of substrate to the MOF-electrolyte interface can be addressed by immobilizing the MOF on a gas diffusion electrode (GDE); the continuous flow of substrate through the permeable electrode removes the limitation by mass transport of poorly soluble, gaseous reactants such as CO_2 (0.00033 mol/L in water) and O_2 (0.00122 mol/L in water). Mass transport inside the MOF pores, however, can be more difficult to study. Rotating ring disc electrode experiments are often performed to study mass transport limitations towards the electrode, but the influence of rotating the electrode on mass transport within a MOF immobilized on this electrode is unknown. The group of Morris achieved independent quantification of electron hopping and ion migration through MOF pores using the Scholz method,[4,5] and subsequently identified pore-size dependency of mass transport: larger pores showed more facile transport of ions.[6] However, the Scholz method relies on accurate measurement of the length of the three-phase junction between the MOF, the electrode and the electrolyte, which is difficult for a solvothermically grown thin film and impossible for a drop casted MOF. To the best of our knowledge, electron transfer and mass transport rates as a function of pore size have not been studied in aqueous electrolyte nor during a catalytic reaction. Thus, knowledge on electrocatalytic MOFs does not include the effect of pore size on catalytic rates.

Quantification of electrochemical processes in MOFs is complicated by the lack of developed theory for MOFs. The mathematics for determination of, for example, electron transfer kinetics (k_{ET}) and catalytic rates (TOF_{max}) is developed for either homogeneous catalysis or heterogeneous catalysis.[7,8] MOFs are porous structures in which diffusion processes take place that fit neither the homogeneous nor the heterogeneous models. Therefore, the development of equivalent methods to the foot-of-the-wave analysis (FOWA), and the Nicholson method that are applicable to catalytic sites embedded in MOFs, would allow for better quantification of electron transfer and catalytic rates. As a result, comparing MOF-embedded catalysts to their homogeneous equivalents would be more meaningful. As described before, efforts have been made, by the groups of Ott, Morris and Dinca amongst others, to study electron transfer mechanisms and rates in MOFs on a fundamental level. Furthermore, there is a large number of application reports on electrocatalytic MOFs. The next step in MOF catalysis should be to translate the understanding of electron transfer mechanisms through the MOF to catalytic performance. Furthermore, structure-activity relationship studies of MOF-embedded catalysts can aid in the development of better-performing electrocatalytic MOFs.

6.3 References

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