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Visualization of local electrocatalytic activity of metalloporphyrins towards oxygen reduction by means of redox competition scanning electrochemical microscopy (RC-SECM)

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ABSTRACT

The redox competition mode of scanning electrochemical microscopy (RC-SECM) has been utilized to visualize the local electrocatalytic activity of metalloporphyrin spots towards oxygen reduction in 0.1 M phosphate buffer as electrolyte solution. The metalloporphyrin spots were obtained by electrochemically induced deposition using a droplet cell. Tetratolyl porphyrins (TTPs) of Mn, Fe and Co have been investigated, with that containing Mn as central metal atom showing highest catalytic activity. The multiple stable oxidation states of Mn were seen as a key factor in the influence of the metal ion on the catalytic activity. From the RC-SECM results, it is shown that oxygen reduction at a manganese TTP (MnTTP) modified electrode surface yielded the least amount of H_2O_2 when compared to iron TTP (FeTTP) and cobalt TTP (CoTTP). As further confirmed by means of rotating disc electrode (RDE) measurements this was attributed to the high activity of MnTTP for H_2O_2 reduction.

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1. Introduction

Macrocyclic organic N₄-complexes of transition metals like metalloporphyrins and metallophthalocyanins are known to catalyze a variety of redox reactions. These reactions are found in porphyrincontaining enzymes such as sulfite reductase [1], nitrate reductase, cytochrome c oxidase [2], blue copper oxidases, pseudocatalase [3], photosystem II [4], nitrogenase and hydrogenase [5]. In each case, the enzyme contains one or more coordinatively bound metal atoms in the active site, and in many cases the enzyme may also include active peripheral metal sites. In 1964, Jasinski [6,7] reported that Co porphyrins are able to electrocatalyze the oxygen reduction reaction (ORR). Since then, a large number of papers appeared dealing with the electrocatalytic oxygen reduction using such so-called N₄-chelates, which were summarized in several reviews [8]. The ORR at such complexes which involves a transfer of at least two electrons through the central metal ion to molecular oxygen requires that molecular oxygen is reversibly bound to the central metal ion. This phenomenon further reiterates the importance of the nature of the central metal atom particularly regarding its affinity for oxygen which influences the overall (electro)catalytic activity of the compound under investigation. Co and Fe containing metalloporphyrins have been investigated in combination with carbon nanotubes [9,10], methanol tolerant electrocatalysts [11], in polyaniline complexes [12,13] or as composite catalysts along with other transition metal oxides [14]. While metalloporphyrins containing Co and Fe as central metal ions have been investigated in greater detail, especially for two- and four-electron oxygen reduction reactions, only a few reports on manganese-containing N₄-macrocyclic complexes with respect to their role in ORR [15,16] have been published.

The investigation of the electrocatalytic activity of N_4 macrocyclic metal complexes towards oxygen reduction generally involves electrochemical techniques such as voltammetry and amperometry [11–24]. However, more and more reports appeared that suggested the use of scanning electrochemical microscopy (SECM) in its many modes to evaluate the activity of catalysts [25–28]. For example, the sample generation-tip collection (SG-TC) mode [26] and the tip generation-sample collection (TG-SC) mode of SECM have been used to visualize the activity of catalysts for local O₂ reduction [29,30]. In the TG-SC mode, the SECM tip, which is positioned close to the sample, locally generates O₂, which is subsequently reduced at the sample under investigation. The Faradaic current flowing through the sample is used as the analytical signal to evaluate its local electrocatalytic activity. Recently, the redox

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competition mode of SECM (RC-SECM) where the tip and the sample under investigation are made to compete for the same analyte in solution in a bipotentiostatic measurement has been suggested [31]. In this case, the current at the tip is used as analytical signal. This approach helped to overcome the challenge observed in the TG-SC mode where a significant contribution of the background signal at larger samples limits the possibility of high resolution imaging [29]. In the RC-SECM mode, the local concentration of O₂ in the gap between SECM tip and sample is kept high by applying repetitive water splitting potential pulses to the tip before the determination of O₂ reduction activity. The RC-SECM image is generally obtained in such a manner that the oxygen reduction at the tip will lead to a constant current signal until the tip is scanned across an O₂ consuming site of the sample. This consumption alters the local O₂ concentration and hence the diffusional fluxes of O₂ towards the SECM tip thereby leading to a decrease in the current flow through the tip. The electrocatalytic properties of the sample are therefore reflected by the modulation of the current signal at the SECM tip.

SECM imaging of local O_2 reduction has generally elucidated the local catalytic activity of a sample but does not provide information on the number of electrons involved in the ORR, which is represented by the formed reaction products. The selectivity of a catalytically active sample either towards a 4-electron (respectively sequential 2×2 -electron) reduction of oxygen to H_2O or a 2-electron reduction to H_2O_2 is of high importance for the optimization of potential electrocatalysts. Recently, a sequential dual imaging mode of the SECM was introduced in which it was possible to conduct a simultaneous visualization of both the local electrocatalytic activity and the selectivity of the investigated catalyst [32]. In that approach, two images are simultaneously obtained where one image elucidates the activity of the sample towards oxygen reduction and the other visualizes the produced (if any) H_2O_2 during the ORR.

In a preceding publication [33], we investigated the properties of electrodeposited² metalloporphyrins with respect to their electrocatalytic activity for O_2 reduction and were able to demonstrate the advantages of the electrochemically induced deposition of metalloporphyrins as compared with dip- or drop-coating processes for electrode modification.

In this contribution, SECM is applied to investigate the electrocatalytic behavior of electrodeposited metalloporphyrins films on electrode surfaces towards O_2 reduction. Tetratolyl porphyrins (TTPs) which contain Mn, Fe and Co as central metal ions have been investigated. The impact of the catalyst loading, which was varied during the electrochemical deposition of the metalloporphyrin layers, that of the central metal ion on the catalytic behavior of these metalloporphyrins towards ORR as well as their selectivity towards electrocatalytic reduction of O_2 was investigated. Comparing results from SECM and rotating disc electrode (RDE) measurements made it possible to further elucidate the mechanism of catalytic O_2 reduction.

2. Experimental

2.1. Materials

The metalloporphyrins used (both commercially purchased and locally synthesized) are abbreviated as follows: manganese TTP (MnTTP), iron TTP (FeTTP) and cobalt TTP (CoTTP). KH₂PO₄ was purchased from VWR, Darmstadt, Germany; $K_2HPO_4 \cdot 3H_2O$ from Merck, Darmstadt, Germany; meso-tetratolyl porphyrin-Co(II) (CoTTP) from Porphyrin Systems (Lübeck, Germany). TBABF₄ (tetrabutylammonium tetrafluoroborate) was from Fluka (Buchs, Switzerland); *N,N*-dimethylformamide (DMF) was from J.T. Baker (Deventer, The Netherlands). For the synthesis of metalloporphyrins, substituted benzaldehydes, trifluoroboron etherate (BF₃·OEt₂), tetraphenylchlorophosphate (Ph₄PCl) were obtained from Merck (Darmstadt, Germany). 2,3-Dichloro-5,6-dicyano-pbenzoqui none and pyrrole were purchased from Sigma–Aldrich (Steinheim, Germany). All chemicals were of analytical grade and used as received. MnTTP and FeTTP were prepared from a oneflask synthesis of porphyrins which followed a standard literature protocol [34–38].

2.2. SECM measurements

The SECM instrumentation has been described before [39]. The main components are stepper motor driven x-y-z stages (Owis, Staufen, Germany), a bi-potentiostat (PG 100; Jaissle, Waiblingen, Germany) and an in-house written control software programmed under Visual Basic 6.0 (Microsoft, Unterschleißheim. Germany). All SECM measurements were carried out in 0.1 M phosphate buffer which was prepared by mixing 0.1 M KH₂PO₄ and 0.1 M K₂HPO₄ (1:1) in triply distilled de-ionized water and adjusting the pH value to 7. A buffered solution has been chosen in order to avoid any unwanted influence of pH changes due to the ORR. Pt-microelectrodes ($\emptyset = 25 \,\mu m$) used as SECM tips were fabricated according to an earlier established procedure [40] using Pt wire purchased from Goodfellow (Bad Nauheim, Germany). Other components of the electrochemical cell include a miniaturized Ag/AgCl/3 M KCl reference electrode, to which all potentials in this work refer, a Pt-foil as counter electrode and an indium-tin-oxide (ITO)-coated glass plate.

During the redox competition mode of SECM the sequential pulse profile applied to the SECM tip was: +50 mV for 500 ms (no-effect potential), +1200 mV for 200 ms (O₂ production), -600 mV for 500 ms (O₂ reduction and data acquisition), +1200 mV for 200 ms (O₂ production) and +600 mV for 500 ms (H₂O₂ oxidation and data acquisition).

2.3. Sample preparation

The metalloporphyrin spots were prepared by a pulsed electrodeposition from a 3 mM solution of each metalloporphyrin in 0.1 M TBABF₄ in DMF. The spots were deposited on a Sigradur® (HTW Hochtemperatur-Werkstoffe, Thierhaupten, Germany) glassy carbon (GC) plate in a specially designed electrochemical droplet cell composed of a Pt wire as counter electrode and a Ag/AgCl/3 M KCl electrode as reference electrode, adapted from the work of Hassel et al. [41]. Each pulse applied in the droplet cell for the electrochemical deposition of the metalloporphyrin followed a sequential potential profile of 0V for 2s, 1.6V for 3s and 0V for 2s. In our previous work, the number of pulses was varied between 10, 20, 30 and 50 pulses to control the catalyst loading on the GC plate, and 20 pulses turned out to be the optimum [33]. Thus, 20 deposition pulses were used if not otherwise stated throughout the study. Since the electrodeposition occurs via ring oxidation, and the ring system is the same in all systems, we assume that similar amounts of porphyrin are deposited in all cases. This is further supported by the similarity of the CVs obtained on the various metalloporphyrins in the potential region where ring oxidation takes place [33]. The metalloporphyrin spots were left to dry briefly and the GC plate was rinsed carefully with DMF to remove loosely attached material. The spot was then left to air-dry. Fig. 1 shows a schematic representation of the electrochemical droplet cell.

² Very often the term "electropolymerization" can be found in literature for the electrochemical deposition of metallo-porphyrins and -phthalocyanins. In this paper, however, the more general term "electrodeposition" is used. In this electrodeposition, likely first a radical cation is formed by oxidation, which attacks a second porphyrin to form a dimer and so on. The exact structure and mechanism, however, is not clear.



Fig. 1. Scheme of the electrochemical droplet cell for the electrodeposition of metalloporphyrins.

2.4. RDE measurements

For the RDE measurements, O₂ reduction at the modified electrode was monitored in O₂ saturated (by bubbling O₂ gas through the solution for 15–20 min) 0.1 M phosphate buffer at pH 7 (see Section 2.2). Using linear sweep voltammetry (LSV), a classical three-electrode configuration comprising a 1 mm Pt wire counter electrode, a Ag/AgCl/3 M KCl reference electrode and the metalloporphyrin modified 3 mm glassy carbon working electrode was used. A potential window from +0.7 V to -0.7 V at a scan rate of 5 mV s⁻¹ was employed. All RDE measurements were carried out using an Autolab PGSTAT12 (Eco Chemie, Utrecht, The Netherlands) potentiostat. The 3 mm glassy carbon working electrode was rotated at rotation speeds of 100, 400 and 900 rpm by an analytical rotator, model ASR2 (Pine Instrument Company, Grove City, PA, USA).

3. Results

3.1. The effect of sample potential

A combination of the TG-SC, SG-TC and RC-SECM modes has been employed in order to visualize the local electrocatalytic activity of metalloporphyrin-modified glassy carbon surfaces. The working principles of this combination have been previously described in detail [32]. Using this combination it is possible to visualize sequentially in a single scan on the one hand the local O₂ consumption of a catalytically active surface and on the other hand the H₂O₂ produced during the ORR. The GC plate upon which the sample is electrochemically deposited is polarized at a potential E_s which is negative enough to provoke O_2 reduction at the sample. A schematic representation of the reactions taking place in the space between the tip and the sample is shown in Fig. 2. The tip is positioned at a z-distance of about 10 μ m away from the sample (using SECM approach curves in the feedback mode). Thus, the SECM tip forms a local thin-layer cell together with the sample surface hindering diffusion of redox species to or from bulk solution.

The sample potential, E_s , has been varied (-600, -400 and -200 mV) in order to investigate the effects of E_s on the observed catalytic ORR activity. The influence of E_s on the catalytic activity as observed in the RC-SECM image is displayed in Fig. 3. O₂ reduction over the metalloporphyrin spots can already be observed at a sample potential of -200 mV. As expected, the observed catalytic activity for ORR increases at more negative sample potentials. At -600 mV a good contrast between the active spot and the significantly less active non-modified GC surface is obtained. The



Fig. 2. Schematic representation of the reactions taking place in the gap between the SECM tip and the metalloporphyrin-modified sample during the redox competition mode of SECM in which the SECM tip and the sample compete for the available O_2 . Note that the tip current during oxygen reduction is also influenced by the amount of H_2O_2 available.

observed small current signal at less negative E_s above the spot indicates a small but almost insignificant contribution from the topography of the electrodeposited metalloporphyrin spot.

3.2. Effects of catalyst loading on catalytic activity

In the pulsed electrodeposition formation of the metalloporphyrins spots, the number of pulses has been varied between 20, 30 and 50 leading to increased thickness of the metalloporphyrin deposit. Using MnTTP as a test sample, the baseline corrected RC-SECM line scans obtained from these deposits are displayed in Fig. 4. Obviously, the electron transfer process using a film formed by 20 pulsed deposition cycles showed highest activity. This is in agreement with earlier work on CV investigations on similar electrochemically deposited metalloporphyrin films [33]. Higher metalloporphyrin loadings thus do not necessarily lead to higher overall catalytic activity. One reason for this behavior might be the semi-conducting properties of the porphyrin film.

3.3. Effects of central metal ion on catalytic activity

The electrocatalytic reduction of O_2 at a metalloporphyrin depends largely on the central metal ion because the ORR occurs by a transfer of electrons via the central metal when bound reversibly to O₂. Other factors such as the electron withdrawing or donating nature of the ring substituents on the porphyrin macrocycle also contribute to this step. To study the influence of the central metal ion, tetratolyl porphyrins which contain Fe, Co and Mn have been investigated. Fe and Co are better known metals in this respect but the multiple stable oxidation states of Mn deserve closer attention. Using the already established electrodeposition parameters (Section 3.2) FeTTP, CoTTP and MnTTP were electrochemically deposited using the electrochemical droplet cell. The catalyst spots were scanned using the RC-SECM mode to elucidate their catalytic activity towards O₂ reduction (Fig. 5). The observed current differences represent the changes in local O₂ concentration which is supposed to be indicative of the local catalytic activity of the metalloporphyrin-modified surface. Due to the fact that the ring substituents for all investigated metalloporphyrins are the same, the central metal atom has obviously a severe influence on the observed local tip current. From Fig. 5 it appears that electrodeposited MnTPP is the most active catalyst, followed by FeTPP, while surprisingly CoTPP exhibits only a low activity. This is unexpected given the fact that Co porphyrins are known O₂ reduction catalysts.

3.4. Selectivity for oxygen reduction

Simultaneously with the investigation of the activity for local O_2 reduction, H_2O_2 production has been visualized by applying



Fig. 3. RC-SECM images showing the effects of sample polarization potential (E_s) on the electrocatalytic O₂ reduction for an electrochemically deposited MnTTP spot. Sample was polarized at -200, -400, and -600 mV, respectively. Color contrasts correspond to the measured cathodic tip current. Lighter and elevated areas correspond to lower negative O₂ reduction current which is indicative of higher electrocatalytic activity at the sample (0.1 M phosphate buffer, pH 7, 25 μ m Pt tip, tip-to-sample distance 10 μ m, data acquisition after 500 ms of the detection pulse).

a sequential pulse profile to the SECM tip as described in Section 2.2. Following the O_2 injection pulse the tip potential is switched to 600 mV to invoke H_2O_2 oxidation. Hence, an anodic current is expected at the SECM tip assuming that H_2O_2 which is formed during the ORR will diffuse across the gap from the sample to the SECM tip following a substrate generation-tip collection scheme. SECM images for H_2O_2 production detected during the ORR are displayed in Fig. 6 for all three metalloporphyrin spots used in this study.

Surprisingly, H_2O_2 detection gave rise to a negative tip current. For a better visibility, the H_2O_2 signal obtained over the MnTPP spot has been inverted. It is note worthy that the GC plate upon which the spot is deposited also reduces O_2 in a 2-electron transfer reaction to H_2O_2 at the applied sample potential of $E_s = -600$ mV. During the scanning procedure, the H_2O_2 produced from the GC surround-



Fig. 4. Baseline corrected RC-SECM *x*-line scans (at $y = 1100 \mu$ m) of electrochemically deposited MnTTP spots at different deposition cycles for the formation of the MnTPP deposit (0.1 M phosphate buffer, pH 7, $E_s = -600$ mV, data acquisition after 500 ms of the detection pulse).

ing the metalloporphyrin spot diffuses to the SECM tip where it is oxidized yielding an increased background current. Whether the GC plate produces more H_2O_2 than the catalyst spot or not will therefore determine the observed current difference which is plotted in the SECM images. A small amount of H₂O₂ produced thus would lead to a current lower than that observed over the unmodified GC surface. If the metalloporphyrin spot however produces more H_2O_2 than the bare GC, the observed current signal over this spot will be positive. Since the scans for all investigated metalloporphyrins lead to a lower current in H₂O₂ production than the GC surface, but a higher O₂ reduction current, it can be deduced that all metalloporphyrin spots produce less H₂O₂ at the used sample potential than the bare GC surface. This can serve as a first indication that O₂ reduction over the electrochemically deposited metalloporphyrin spots does not occur according to a simple 2-electron transfer mechanism under formation of H₂O₂. It can be assumed that the primarily formed H₂O₂ is further reduced to H₂O at the metalloporphyrin-modified sample while H₂O₂ formed at the nonmodified GC surface is not further reduced and can hence diffuse to the SECM tip. Alternatively, O_2 may at least in part (e.g. at some special active sites) be reduced in a 4-electron transfer reaction to H_2O_2 , thus circumventing the formation of H_2O_2 .

In order to verify these assumptions, the RC-SECM experiments were repeated but this time on a conducting surface which has a high overpotential with respect to O_2 reduction. An ITO coated glass slide was modified with 5% (v/v) dimethlydichlorosilane in CHCl₃ to increase the hydrophobicity of the surface. Metalloporphyrin spots were electrodeposited on the ITO coated glass slide using the droplet cell. In Fig. 7, the related RC-SECM images obtained both in the O_2 reduction and the H_2O_2 detection potential pulse sequence is shown. As expected, the current obtained above the metalloporphyrin spot due to the oxidation of H_2O_2 at the SECM tip is now positive. The amount of H_2O_2 is lowest over the MnTPP spot and highest over the CoTPP-modified surface. The latter fact is note worthy keeping in mind the low activity for O_2 reduction at the electrodeposited CoTPP spot observed during the RC-SECM measurements (see Fig. 5). Even though ITO proved to be the better



Fig. 5. (A) RC-SECM O₂ reduction images of FeTTP, CoTTP and MnTTP spots. Color contrasts correspond to the measured cathodic tip current. (B) Baseline corrected *x*-line scans (*y* = 1100 μm) at each sample (sample polarized at -600 mV, 0.1 M phosphate buffer, pH 7, 25 μm Pt tip, tip-to-sample distance 10 μm, data acquisition after 500 ms of the detection pulse).

substrate for H_2O_2 detection, further experiments with ITO have not been carried out due to low adhesion of the electrodeposited film, causing severe experimental problems, and only rarely a sample was stable for the duration of an SECM experiment.

3.5. RDE measurements

In order to further confirm the applicability of RC-SECM in the investigation of the electrocatalytic activity of metalloporphyrins towards O_2 reduction, an RDE was used for voltammetric measurements under controlled mass-transfer conditions. The metalloporphyrins were electrochemically deposited on 3 mm diameter GC electrodes. The electrochemical deposition of the metalloporphyrins was done by applying a single pulse at 1.6 V for 90 s. Different deposition parameters compared to the SECM measurements have been used since it turned out that the procedure established for the droplet cell did not yield satisfactory results in the case of direct electrodeposition on the 3 mm GC rods. After deposition, the electrodes were carefully rinsed by dipping in triply distilled water and allowed to air-dry before use. Linear sweep voltammogramms were recorded at 100, 400 and 900 rpm and the curves subjected to the standard Koutecky-Levich analysis resulting in the calculated kinetic current. A plot of the logarithmic kinetic current density against the potential (Tafel plot) for the different metalloporphyrin films is displayed in Fig. 8. In this case and in contrast to the results from RC-SECM measurements, the CoTPP exhibits the highest catalytic activity for O₂ reduction. As can be seen, the Tafel plots show certain nonlinearity. This is due to the fact, that the number of active sites involved in the ORR differs with potential. While at less negative potentials, the oxygen is supplied to the whole film, leading to a linear Tafel plot, at more negative potentials (i.e., with a highly active catalyst) all the oxygen is reduced at the outer layer of the thin film. Thus, at more negative potentials less active sites are involved, leading to a virtual decrease in activity and a nonlinearity of the Tafel plot.

From the Koutecki–Levich plots (see supplementary information, determined at -0.4 V), the average number of electrons transferred for each of the electrodeposited films has



Fig. 6. (A) H₂O₂ oxidation above electrochemically deposited FeTTP, CoTTP and MnTTP spots during ORR. H₂O₂ produced at the sample is oxidized at the tip at a potential of +600 mV. The H₂O₂ oxidation current above the catalyst spot is a relative value to that at the bare glassy carbon surface. These images were obtained sequentially in the same RC-SECM scan with those shown in Fig. 5 under the same experimental conditions. For better visibility the tip current values were inverted for the MnTTP spot. (B) Baseline corrected *x*-line scans at each sample (sample polarized at -600 mV, 0.1 M phosphate buffer, pH 7, 25 µm Pt tip, tip-to-sample distance 10 µm, data acquisition after 500 ms of the detection pulse).

been calculated to be approximately 3.5 for MnTTP, 2.2 for CoTTP and 3.7 for FeTTP. From these values, it is clear that O_2 reduction at CoTTP favors the 2-electron transfer process, hence producing exclusively H_2O_2 as already observed in the SECM experiments.

When comparing RC-SECM with RDE results, there seems to be an inconsistence. With both methods, the detected activity of the MnTPP and FeTPP deposits was similar. However, in contrast to RC-SECM, RDE measurements showed CoTPP to be the most active catalyst for ORR. Both methods, however, qualitatively agree in the observation that CoTPP produces much more H_2O_2 during O_2 reduction than do the other two metalloporphyrins. To explain these differences, a microscopic picture of the processes occurring in the gap between tip and sample has to be envisaged (see Fig. 2). In the case of a complete reduction of O_2 to H_2O , which is nearly achieved over MnTPP, the case is rather simple: the amount of O_2 in the gap between sample and tip is lowered due to consumption by MnTPP, thus the tip current is lowered which reflects the catalytic activity of MnTPP. In the case of an incomplete reduction of O_2 , however, as in the case of CoTPP, H_2O_2 accumulates in the gap between tip and sample. Here, not only the remaining O_2 is reduced at the tip but also the produced H_2O_2 . Thus the current at the tip is higher than it should be if only the remaining O_2 was contributing, thus indicating an apparent lower consumption of O_2 by the sample and hence a lower activity for ORR.

Furthermore, in this case the metalloporphyrin spot is continuously exposed to higher H_2O_2 concentrations since the sample potential is applied throughout the whole experiment. A deterioration of the metalloporphyrin film by H_2O_2 can be assumed leading additionally to a decreased catalytic activity of CoTPP with respect to ORR as seen in the RC-SECM experiment. Preliminary experiments, in which a CoTPP film has been exposed to a 3.3 M H_2O_2 solution for 40 min, indeed showed a decrease in activity.



Fig. 7. RC-SECM images of electrocatalytic O₂ reduction at an electrochemically deposited MnTTP spot on an ITO coated glass slide. The images were obtained under the same experimental conditions as for the images displayed in Fig. 5. (A) O₂ reduction and (B) H₂O₂ oxidation (sample polarized at -600 mV, 0.1 M phosphate buffer, pH 7, 25 μm Pt tip, tip-to-sample distance 10 μm, data acquisition after 500 ms of the detection pulse).

3.6. H₂O₂ reduction

As derived from the RDE measurements (see Fig. 8), MnTPP showed an average number of 3.5 electrons per reduced O_2 molecule. Additionally, the MnTPP spot showed the lowest H_2O_2 oxidation current in the RC-SECM measurements (see Fig. 6). As pointed out above, besides an intrinsically improved selectivity of the MnTPP for ORR following a 4-electron transfer pathway, a sequential electron transfer under intermediate formation of H_2O_2 can equally explain the observed results. In this case, the multiple stable oxidation states of the Mn porphyrin may exhibit a facilitated further reduction of H_2O_2 , potentially even immediately after its formation. Control experiments were run to verify this hypothesis. CoTTP and MnTTP films were electrochemically deposited on 3 mm GC electrodes using the established protocol and the films obtained



Fig. 8. Tafel plots displaying the electrocatalytic activity towards O_2 reduction on glassy carbon electrodes which were modified with electrodeposited (a) FeTTP, (b) CoTTP and (c) MnTTP (0.1 M phosphate buffer, pH 7).



Fig.9. Linear sweep voltammograms showing the electrocatalytic reduction of H_2O_2 in deaerated 1 M H_2O_2 in 0.1 M phosphate buffer at (a) CoTTP and (b) MnTTP films. Scan rate: 50 mV s⁻¹.

were tested for H_2O_2 reduction in 1 M H_2O_2 in 0.1 M phosphate buffer solution while excluding O_2 by purging the solution with Ar for about 20 min before the experiment. Fig. 9 shows the reduction of H_2O_2 at MnTTP and CoTTP films in the absence of oxygen. The results revealed that MnTTP is indeed significantly more active for H_2O_2 reduction even at the same oxygen reduction potential. This confirms that the MnTTP spot is able to further reduce H_2O_2 to H_2O .

4. Conclusion

The redox competition mode of scanning electrochemical microscopy is a versatile tool in investigating the local electrocatalytic activity of surface immobilized O₂ reduction catalysts. Here, its application has been successfully extended to electrodeposited films of Co, Fe and Mn porphyrins. Mn porphyrins show a high selectivity towards water formation in oxygen reduction. The effects of catalysts loading and central metal ion on the catalytic activity of metalloporphyrins towards O₂ reduction have been demonstrated by RC-SECM measurements with comparable results to those obtained from RDE measurements. Furthermore, SECM has been shown to be a tool to obtain information on the selectivity in oxygen reduction and might thus complement RRDE measurements. Future work will be directed towards the investigation of a larger library of metallo N₄-macrocycles with respect to electrocatalytic activity and selectivity for ORR and a more detailed elucidation of the influence of the pH-value on the electrocatalytic activity of electrodeposited metalloporphyrin films.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2009.02.047.

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