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Controlling Proton and Electron Transfer Rates Enhances the Activity of an Oxygen Reduction Electrocatalyst

Rajendra P. Gautam, Yi Teng Lee, Gabriel L. Herman, Cynthia M. Moreno, Edmund C. M. Tse, and Christopher J. Barile*

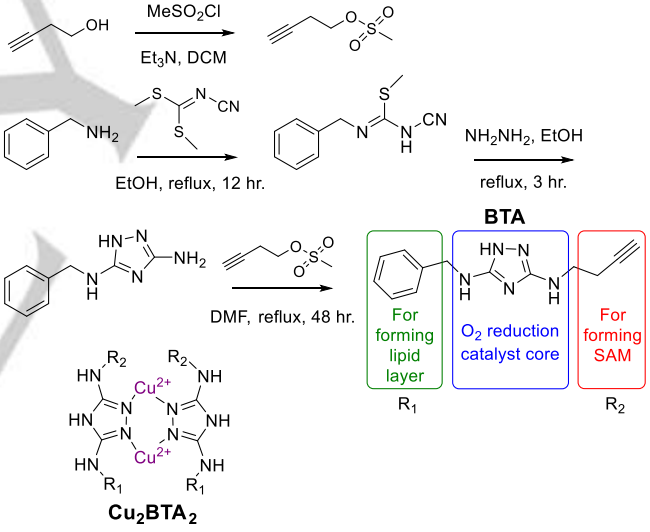
Abstract: Reactions involving proton and electron transfer are fundamental to many chemical and biological processes. Here, we develop an electrochemical approach that allows for the control of both proton and electron transfer rates in the O_2 reduction reaction (ORR). We prepared a dinuclear Cu ORR catalyst that can be covalently attached to thiol-based self-assembled monolayers (SAMs) on Au electrodes using azide-alkyne click chemistry. Using this architecture, the electron transfer rate to the catalyst is modulated by changing the length of the SAM, and the proton transfer rate to the catalyst is controlled with an appended lipid membrane modified with proton carriers. By tuning the relative rates of proton and electron transfer, we enhance the current density of the lipid-covered catalyst without altering its core molecular structure. We envision that this type of electrochemical platform will aid in identifying the optimal thermodynamic and kinetic parameters not only for ORR catalysts, but for catalysts of other reactions that involve the transfer of both protons and electrons.

Reactions involving the transfer of multiple protons and electrons are instrumental in many renewable energy conversion schemes and biological processes.[1-7] One of the most important redox reactions that involves proton transfer is the O_2 reduction reaction (ORR), which occurs at the cathode of fuel cells and in mitochondria present in all aerobic life.[8-11] Unfortunately, the mechanistic details of the ORR are difficult to elucidate because of the complex interplay between the thermodynamics and kinetics of the multiple proton and electron transfer steps involved.[12]

In this work, we design an electrochemical platform that allows for the control of the thermodynamics and kinetics of proton and electron transfer to a Cu-based molecular ORR catalyst. It is well known that the electrode potential dictates the thermodynamics of electron transfer and that the pH of the bulk solution controls the thermodynamics of proton transfer in many metal-centered proton transfer reactions.[13-16] The kinetics of electron transfer can be modulated to a molecular catalyst through the use of self-assembled monolayers (SAMs) with varying alkyl chain lengths.[17-19] However, there are few methods to control the kinetics of proton transfer to a catalyst in an unconvoluted manner. Gewirth and coworkers recently developed proton-permeable lipid membranes to alter the proton transfer kinetics to a catalyst without perturbing its molecular identity.[20,21] These membranes contain amphiphilic alkyl proton carriers that deliver protons via a flip-flop diffusion process.[22]

Here, we develop an electrode architecture containing an ORR catalyst that allows for both the control of proton transfer rates through the use of lipid membranes and the control of electron transfer rates through the use of a modular SAM scaffold that takes advantage of azide-alkyne click chemistry. The click chemistry approach enables us to attach a synthesized ORR catalyst to a SAM surface. The length of the catalyst-modified SAM can be facilely modified without changing the identity of the catalyst. Together, this click platform provides a means to control electron transfer kinetics to the catalyst. By altering the amount of proton carrier in the lipid layer of the same platform, proton transfer kinetics can also be tuned.

We first designed a ligand that supports an active ORR catalyst that can be incorporated into an electrode architecture with tunable proton and electron transfer kinetics. The ligand, N^3-benzyl-N^5-(but-3-yn-1-yl)-1*H*-1,2,4-triazole-3,5-diamine (BTA), was synthesized in four steps from benzylamine and contains three important features (Scheme 1). First, the BTA ligand contains a diaminotriazole core which upon coordination to Cu forms a highly active ORR catalyst. This core is inspired by previous studies with a dinuclear Cu complex of 3,5-diamino-1,2,4-triazole, which in terms of overpotential is one of the most active molecular Cu ORR catalysts known.[23-25] Second, BTA contains an alkyne moiety, which allows it to undergo the azide-alkyne click reaction with azide-terminated SAMs. Lastly, BTA possesses a benzyl group, which enables lipid monolayers to assemble on top of a BTA SAM.[20] The hydrophobic tails of the lipid monolayer are appended to the hydrophobic benzyl groups of the BTA SAM via Van der Waals interactions.



Scheme 1. Synthesis of BTA with three important features highlighted along with the structure of the dinuclear CuBTA complex.

Electrodes containing the CuBTA ORR catalyst with tunable proton and electron transfer rates were constructed in three steps (Figures 1 and S1). First, Au electrodes were modified with SAMs of azide-terminated thiols with different alkyl chain lengths. Next, the BTA ligand was covalently attached to the SAM using azide-alkyne click chemistry and subsequently immersed in a Cu^{2+} solution to form the active dinuclear Cu complex. Lastly, a lipid monolayer containing 1-dodecylboronic acid (DBA) as a proton carrier was appended on top of the SAM to complete the electrode architecture.

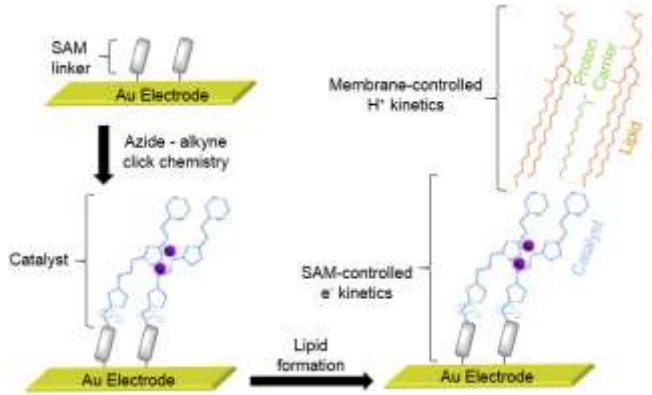


Figure 1. Schematic of the fabrication of lipid-modified SAMs used to control the electron and proton transfer rates to a molecular O_2 reduction catalyst.

Electrochemical techniques were used to assess the chemical structure of the electrodes at each fabrication stage. Electrodes containing the CuBTA catalyst were first assembled using an azide-terminated thiol containing 5 methylene groups (Figures 1 and S1, n = 5). The presence of Cu in the catalyst was confirmed by a Cu(I)/Cu(II) couple in cyclic voltammetry (CV) experiments (Figure S2). By integrating the charge of the Cu couple in the CV, the amount of Cu catalyst on the surface was determined to be 1.3 x 10^{-11} mol cm^{-2}, a value that matches what is expected for a full monolayer of Cu (see SI). A linear sweep voltammogram (LSV) of the CuBTA assembly without a lipid layer demonstrates that CuBTA is an active ORR catalyst that exhibits an onset potential of about 0 V vs. Ag/AgCl and an O_2 diffusion-limited peak current density of about -900 μA cm^{-2} in O_2-sparged pH 7 buffer (Figure 2, black line). Control experiments in the absence of O_2 (Figures 2 and 3, dashed lines), with Zn, or without performing the click chemistry do not exhibit significant ORR activity, further demonstrating that Cu is necessary to produce an active catalyst (Figures S3 and S4). Further control experiments comparing the activity of Cu complexes of 3,5-diamino,1,2,4-triazole and 1,2,3-triazole indicate that the Cu-1,2,3-triazole complex is not a competent ORR catalyst, demonstrating that the 1,2,3-triazole linker formed from the azide-alkyne click chemistry is not contributing to the ORR activity measured (Figure S5).

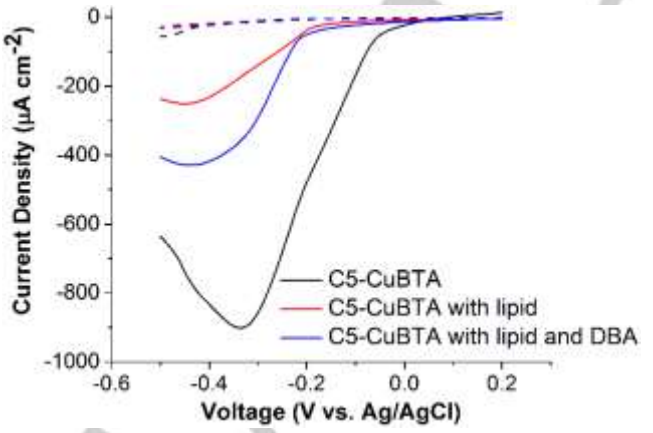


Figure 2. Linear sweep voltammograms of O_2 reduction by the CuBTA catalyst using an azide-terminated thiol SAM containing 5 methylene groups (black line) covered by a DMPC lipid monolayer (red line) with 10 mol% DBA proton carrier (blue line) at 10 mV/s in O_2-saturated pH 7 buffer. Dashed lines are the corresponding voltammograms in N_2-saturated pH 7 buffer.

Having established that the CuBTA complex catalyzes the ORR, we next evaluated the ORR activity of CuBTA when the SAM is covered by a monolayer of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) lipid. A LSV of CuBTA in the presence of lipid displays an onset potential of about -0.2 V and a peak current density of about -250 μA cm^{-2} (Figure 2, red line). The negative shift in onset potential and reduction in current density indicates that the ORR activity of CuBTA significantly decreases upon lipid formation. This inhibition of catalytic activity arises from impeded proton transport across the hydrophobic lipid membrane as has been observed in other lipid-covered electrodes[26] and is also manifested by an about 50 mV negative shift in the midpoint potential of the Cu(I)/Cu(II) couple (Figure S2). O_2 diffusion through the lipid monolayer is fast, and hence the ORR by lipid-covered CuBTA is not limited by a lack of O_2 (Figure S6). Results obtained from electrochemical impedance spectroscopy demonstrate that the molecular length of the system increases upon performing the click reaction and further increases upon lipid formation, as expected (Figure S7). Upon incorporating the DBA proton carrier in the lipid, the CuBTA catalytic current density increases to about -425 μA cm^{-2}, but the onset potential does not change considerably (Figure 2, blue line). This result demonstrates that the presence of the proton carrier enhances the kinetics of the ORR without significantly altering the thermodynamics of the reaction. The peak in the LSV in the presence of lipid and proton carrier is due to kinetically-limited proton transfer. DBA delivers protons across the lipid membrane via flip-flop diffusion in a kinetically-controlled fashion as discussed previously.[21] Electrochemical blocking experiments using $Fe(CN)_6^{3-}$ demonstrate that the ORR does not compromise the integrity of the lipid layer regardless of whether the proton carrier is present (Figure S8).

To modify the electron transfer kinetics to the CuBTA catalyst, we changed the SAM to an azide-terminated thiol containing 11 methylene groups (Figures 1 and S1, n = 11). As measured using Laviron analysis[27] (Figure S9), this longer-chained SAM, which possesses a greater barrier for electron tunneling, exhibits about 30 times slower electron transfer than the previously described thiol containing 5 methylene groups ((1.2 ± 0.2) s^{-1} and (39 ± 3) s^{-1} for the C_{11} and C_5 SAMs, respectively). A LSV of O_2 reduction by CuBTA attached to the C_{11} SAM displays an onset potential of about 0 V and a peak current density of about -275 μA cm^{-2} (Figure 3, black line). The onset potentials for ORR using C_{11} and C_5 SAMs are similar because the active catalyst is the same in both cases, which means that the thermodynamics for catalyzing the ORR do not change when altering the SAM. However, the peak current density is significantly less for the C_{11} SAM due to the slower electron transfer rate. Also, the Tafel slope of the LSV for the C_{11} SAM is significantly higher than that of the C_5 SAM, further indicating that electron transfer kinetics are impeded in the C_{11} case (Figure S10). Upon covering the C_{11}-linked catalyst with lipid, the current density decreases and the onset potential shifts negative in a manner similar to what is observed with the lipid-covered catalyst on C_5 SAM (Figure 3, red line). Incorporation of the proton carrier also enhances the

catalytic current, but does not significantly alter the onset potential for catalysis (Figure 3, blue line). In short, similar changes in the ORR voltammetry occur using both the C_{11} and C_5 SAMs, but the slower electron transfer rate for the C_{11} SAM decreases the overall kinetics of catalysis.

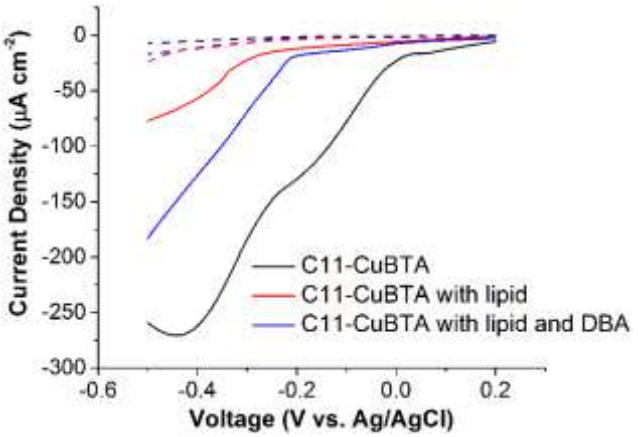


Figure 3. Linear sweep voltammograms of O_2 reduction by the CuBTA catalyst using an azide-terminated thiol SAM containing 11 methylene groups (black line) covered by a DMPC lipid monolayer (red line) with 10 mol% DBA proton carrier (blue line) at 10 mV/s in O_2-saturated pH 7 buffer. Dashed lines are the corresponding voltammograms in N_2-saturated pH 7 buffer.

To complement the modulation of electron transfer rates using SAMs, we also varied the proton transfer rate to the CuBTA catalyst by changing the concentration of proton carrier in the lipid layer. The data in Figure S11 show that as the amount of proton carrier in the lipid layer increases, the current enhancement afforded by the lipid layer compared to the lipid-only case correspondingly increases. The current enhancement observed saturates when around 10 mol% of proton carrier is added to the lipid membrane, which is the maximum amount of DBA that can incorporate in the lipid during vesicle formation.[21] Since proton transfer rates across this lipid membrane have already been measured (Figure S12),[21] we calculated the ratio of the proton and electron transfer rates to CuBTA (k_{H+}/k_{e-}). The ORR current density enhancement by the proton carrier increases as a function of k_{H+}/k_{e-} (Figure 4). In the absence of the proton carrier, proton transfer to the catalyst is almost entirely blocked by the hydrophobic lipid layer, and as a result, the 1 e^- reduction of O_2 to superoxide predominantly occurs.[28] With added proton carrier, k_{H+}/k_{e-} increases, which favors the 4 e^- reduction of O_2 to H_2O as evidenced by dye-based spectroelectrochemical experiments quantifying the amount of partially reduced oxygen species (Figure S13) and results in increased current density (Figure S14). Therefore, the addition of proton carrier changes the rate-determining step (RDS) for the ORR. In particular, the RDS changes from electron transfer with lipid in the absence of proton carrier to proton transfer in the presence of proton carrier as discussed previously.[20] The use of both the C_{11} and C_5 SAMs with different electron transfer rates allows for two orders of magnitude of k_{H+}/k_{e-} to be accessed. The current enhancement using the C_{11} SAM is greater than the enhancement measured on the C_5 SAM regardless of the amount of proton carrier in the lipid layer (compare black points to red points, Figure 4). The greater enhancement with the C_{11} SAM occurs because the accelerated proton transfer rate with the proton carrier has a larger relative impact on the catalytic current density when the electron transfer rate to the catalyst is slow. In contrast, with a C_5 SAM in which relatively fast electron transfer occurs, the proton carrier's ability to enhance the ORR activity is not as pronounced. Strikingly, the current density enhancements are similar for the C_5 SAM with the maximum amount of proton carrier (10 mol%) and the C_{11} SAM with the minimum amount of proton carrier (0.2 mol%) because the two cases have similar k_{H+}/k_{e-} values (compare rightmost red point and leftmost black point, Figure 4). These results demonstrate that the interplay between proton and electron transfer rates dictates the overall activity of the ORR catalyst. We note that relative changes in the peak current density do not strictly reflect changes in the catalytic rate due to small shifts in the position of the peaks, but these effects are minimal.

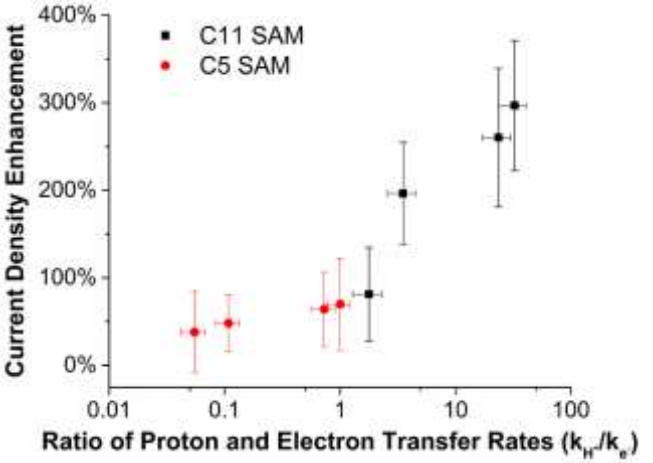


Figure 4. O_2 reduction current density enhancement by CuBTA imparted by the incorporation of the DBA proton carrier in the lipid as a function of the ratio of proton and electron transfer rates (k_{H+}/k_{e-}) using an azide-terminated thiol SAM containing 5 (red points) and 11 (black points) methylene groups.

To the best of our knowledge, this work is the first example of an electrochemical platform that allows for the quantitative control of both the electron and proton transfer rates to a single molecular catalyst without changing its identity. For the CuBTA ORR catalyst studied here, tuning the relative rates of proton and electron transfer enable the catalytic activity to be substantially enhanced by (297 ± 73)% compared to the lipid-only case. We envision that this sort of electrode scheme will enable researchers to elucidate the kinetic parameters needed for optimal catalysis, not only for the ORR, but for any reaction involving the transfer of protons and electrons.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: oxygen reduction • self-assembled monolayer • electrocatalyst • proton and electron transfer • voltammetry

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