O₂ Reduction at a DMSO/Cu(111) Model Battery Interface

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Abstract

In order to develop a better understanding of electrochemical O₂ reduction in non-aqueous solvents, we apply two-photon photoelectron spectroscopy to probe the dynamics of O₂ reduction at a DMSO/Cu(111) model battery interface. By analyzing the temporal evolution of the photoemission signal, we observe the formation of O₂⁻ from a trapped electron state at the DMSO/vacuum interface. We find the vertical binding energy of O₂⁻ to be 3.80 ± 0.05 eV, in good agreement with previous results from electrochemical measurements, but with improved accuracy, potentially serving as a basis for future calculations on the kinetics of electron transfer at electrode interfaces. Modelling the O₂ diffusion through the DMSO layer enables us to quantify the activation energy of diffusion (31 ± 6 meV), the diffusion constant (1 ± 1·10⁻⁸ cm²/s), and the reaction quenching distance for electron transfer to O₂ in DMSO (12.4 ± 0.4 Å), a critical value for evaluating possible mechanisms for electrochemical side reactions. These results ultimately will inform the development and optimization of metal-air batteries in non-aqueous solvents.

Introduction

O₂ reduction reactions (ORR) are one half of the principle reactions of metal-air batteries, which promise extraordinarily high energy storage density from earth abundant materials. However, numerous issues hinder large scale industrial use, from competing side-reactions at the oxygen reduction electrode that form insulating, insoluble, O₂-containing salts, to high overpotentials for oxygen reduction due to sluggish oxygen reduction kinetics. Developing the precise solvent and electrolyte systems to promote desired reactivity and hinder side-reactions is crucial for developing metal-air battery technology, but often relies upon trial and error methods because we have a limited understanding of the fundamental distances and reaction energies relevant for oxygen reactivity at electrode interfaces.

Dimethyl sulfoxide (DMSO) is a non-aqueous solvent that has attracted attention as a solvent in lithium-, zinc-, and sodium-air batteries because of its role in modifying the energies of critical intermediates of the ORR. It is proposed that DMSO stabilizes O₂⁻ at a distance far enough from the electrode to prevent the formation of O₂²⁻ and the insu-
lating, insoluble, O₂-containing electrode passivation side-products. Molecular dynamics (MD) simulations predict that, immediately after the ORR, O₂ is pushed approximately 10 Å away from the electrode at negative cathode potentials making a second electron transfer unlikely. Determining the thickness of DMSO that prevents electron transfer to O₂, and therefore how far O₂ needs to be away from an electrode to not react, is critical to designing DMSO-based electrolytes for metal-air batteries, but is currently unknown and a focus of this work.

The Marcus theory of electron transfer has been used to predict the kinetics of electron transfer at electrode interfaces. However, successful application of the theory requires accurate information about the energies of donor and acceptor species both before and after electron transfer, such as vertical binding energies and adiabatic electron affinities, to calculate the reorganization energy and energy of reaction that determines the interfacial reaction rate. The relevant energies for O₂ and O₂⁻ in DMSO have been estimated from the O₂/O₂⁻ redox potential in DMSO measured with cyclic voltammetry (CV). The O₂/O₂⁻ redox potential ranges from -0.73 V in a 0.1 M (Et)₄NClO₄-DMSO solution with respect to a standard calomel electrode (SCE) to 2.7 V in a 0.1 M TBAClO₄-DMSO solution versus Li/Li⁺ using in situ surface enhanced Raman spectroscopy (SERS) measurements. These redox potentials can be compared to the vacuum level of the working electrode through the standard hydrogen electrode and its vacuum level (details in the Supporting Information) but result in a fairly wide range of energies as shown in Figure 1(a) (first two columns). These factors make the accurate determination of the vertical binding energy (VBE) of O₂⁻ in DMSO challenging and prevent accurate modeling of electron transfer reactions at electrode surfaces.

Owing to their importance in a variety of research fields, electron solvation processes have been subject of numerous studies in the ultrafast time domain applying optical and terahertz spectroscopy as well as photoemission. Two-photon photoemission (2PPE) spectroscopy of solvent molecular layers has been used to probe the energies, solvation dynamics, and reactivity of electronic states in molecular layers ranging from H₂O, NH₃, and organic solvents like DMSO, to liquid crystals. By using ultrafast laser pulses to create excited electrons above the Fermi level of a metal substrate, non-equilibrium electrons can be injected into adsorbed molecular layers and probed using a second laser pulse delayed by femtoseconds to microseconds. Using this strategy, 2PPE has been able to observe the 10s-100s of femtoseconds formation of small polarons in DMSO. In a previous publication, we discuss the electron transfer from these electronic states located on two wetting monolayers of DMSO to much longer-living electronic states located on thicker DMSO islands with lifetimes on the order of seconds. A cartoon of the transfer process is displayed in Figure 1(b). Furthermore, 2PPE is capable of determining the population dynamics of such long-lived states by applying pump-wait-probe experiments (cf. Supporting Information) or measuring the repetition rate dependence of the respective feature. Even chemical reactions involving long-lived “trapped” electrons can be detected in 2PPE experiments. For example, on water-ice surfaces, it was shown that trapped electrons can react with co-adsorbed molecules, breaking H–OH and Cl–CCl₂F bonds and generating highly reactive hydroxide and chloride ions.

In this paper, we use monochromatic 2PPE of O₂ adsorbed on DMSO molecular layers on Cu(111) to probe the electronic states of DMSO and O₂ at a model electrode interface. We show that trapped electrons of DMSO (P₂ shown in Fig. 1(b)) serve as a precursor for O₂⁻ formation. We measure the VBE of O₂⁻ to be 3.80 ± 0.05 eV.

By investigating the electron transfer dynamics from the trapped electron state in DMSO to O₂, i.e. the first ORR, along with modelling O₂ diffusion into the DMSO adlayer, we can observe the distance dependence of O₂ reduction and identify the reaction quenching distance for electron transfer in DMSO. Through these experiments we have determined two components
critical for accurate models of electrochemical systems with DMSO and O₂, the VBE of O₂ and its formation distance, which will direct research efforts to prevent electrode passivation by unwanted oxygen reduction pathways.

Methods

The Cu(111) crystal is prepared by repeated cycles of sputtering at 0.75 kV with 1.5 × 10⁻⁶ mbar Ar⁺ ions for 10 min followed by annealing at 800 K for 45 min. The surface cleanliness and order is verified by LEED, work function (Φ) measurements, and the width and intensity of the surface state characteristic for Cu(111) in 2PPE spectra. The ≥ 99.9% anhydrous DMSO (Sigma Aldrich) is attached to the gas manifold of the ultrahigh vacuum system in an Argon atmosphere and cleaned by numerous freeze-pump-thaw cycles. Its cleanliness is confirmed by residual gas analysis. The DMSO molecules are deposited onto the copper substrate through a pinhole doser with a diameter of 5 µm and a backing pressure of 6 × 10⁻¹ mbar. First, molecules are deposited for 210 s with the Cu crystal temperature held at 200 K. Afterwards the sample is annealed for ten minutes at 210 K before further molecules are deposited at 150 K for 135 s, followed by a second annealing at 180 K for 10 minutes. As discussed previously, using this method a reproducible adsorption of two crystalline DMSO monolayers partially covered with multilayer islands is achieved and the nominal layer thickness is verified with thermal desorption spectroscopy. More information about sample preparation and characterization of DMSO adlayers can be found in a previous publication and the corresponding Supporting Information. O₂ molecules are adsorbed onto the DMSO/Cu(111) sample by background dosing at 46 K. At this temperature only a monolayer of O₂ can be physisorbed on the surface. All referenced temperatures are measured using a K-type thermocouple inside the copper crystal.

The laser system is a Light Conversion Pharos pump laser combined with a non-linear optical parametric amplifier (Orpheus 2H) operating at 200 kHz. This system delivers ultrashort laser pulses tunable from the visible to near UV. In the described experiments, photon energies between 2.9 eV and 3.2 eV are used, with pulse durations of approximately 100 fs.

Monochromatic 2PPE is a surface-sensitive technique that can determine the energies of both occupied and normally unoccupied electronic states with respect to the Fermi and vacuum level of the sample. The working principle is depicted in Figure 2(a). In 2PPE, the absorption of two photons ionizes the sample and generates photoelectrons with finite kinetic energies with respect to the vacuum level, E_{vac}. The kinetic energies, E_{kin}, of the photoemit-
Figure 2: (a) Monochromatic 2PPE schematic. The green and purple arrows show different photon energies for distinguishing intermediate and initial states in 2PPE spectra. (b) Steady-state 2PPE spectrum of 4 ML of DMSO on Cu(111) with (solid) and without (dashed) O$_2$ adsorption. The shaded red ($P_3$), dark blue ($P_2$), and light blue ($P_1$) curves are Gaussians fitted to the 2PPE spectrum of the O$_2$ dosed sample. (c) Final state energy of $P_2$ and $P_3$ versus photon energy averaged over four different fluences. The error bars refer to the standard deviations of the fits for individual measurements. (d) Energy level alignment for multilayer DMSO on Cu(111) with additional O$_2$ adsorption. After the small polaron ($P_1$, light blue) is formed, the electron can become trapped ($P_2$, dark blue) and react with O$_2$ to form O$_2^-$ ($P_3$, red).

The energy of 2PPE features can be expressed in relation to different reference levels based on the measurement of the kinetic energy of the photoelectrons, the independent determination of $E_F$ and $\Phi$ of the sample: The final state energy, $E_{\text{final}}$ (Figure 2(a), left axis), provides the excess energy of the photoelectrons with respect to $E_F$

$$E_{\text{final}} = E_{\text{kin}} + \Phi$$  \hspace{1cm} (1)

where $E_F$ is determined at a gold surface in electrical contact with the sample. $\Phi$ is given by the half-maximum of the intensity of the 2PPE spectrum’s low-energy cutoff on the final state energy axis as discussed in detail previously. The intermediate and initial state energies, $E_{\text{int}}$ and $E_{\text{int}}$, are measured with a hemispherical electron analyzer (SPECS Phoibos 100).

The energy resolution of the experimental setup is better than 50 meV and determined by the spectral width of the laser pulse and the resolution of the analyzer. If the 2PPE process occurs via a real, normally unoccupied, so-called intermediate state above the Fermi energy, $E_F$, variation of the photon energy by $\Delta h\nu$ will shift the peak by this value in the 2PPE spectra (left in Figure 2(a)). If there is no real intermediate state, and the photoemission intensity results from an occupied initial state below $E_F$, variation of the photon energy by $\Delta h\nu$ will shift the 2PPE peak by $2\Delta h\nu$ (right in Figure 2(a)).
and $E_{\text{ini}}$, respectively, are:

$$E_{\text{int}} = E_{\text{final}} - h\nu$$  \hspace{1cm} (2)

$$E_{\text{ini}} = E_{\text{initial}} - 2h\nu < 0$$  \hspace{1cm} (3)

Finally, the VBE (Figure 2(a), right axis) with respect to $E_{\text{vac}}$ is useful when comparing energy levels to electrochemical data and is calculated by

$$\text{VBE} = \Phi - E$$  \hspace{1cm} (4)

where $E$ either denotes the intermediate or initial state energy, depending on the character of the investigated state, both with respect to $E_{F} = 0$.

## Results

### Energy level alignment of O$_2$-related states

Adsorption of O$_2$ on top of 4 ML of DMSO on Cu(111) modifies the electronic states measured by 2PPE spectroscopy and their energy level alignment. Figure 2(b) shows the monochromatic 2PPE spectra of DMSO/Cu(111) with and without O$_2$ relative to the final (top) and intermediate state energy axis (bottom). The spectrum with O$_2$ (grey) is notably broader to the high-energy side than the one without O$_2$ (dashed), and can be fit with three Gaussian peaks shown in light blue, dark blue, and red and referred to as $P_1$, $P_2$, and $P_3$, respectively. A comparison between the data and the corresponding fit is shown in the Supporting information. $P_1$ at $E_{\text{int}} = 2.8$ eV with respect to $E_F$ is consistent with the transient small polaron in DMSO with the same energy level alignment as in the absence of O$_2$.\textsuperscript{81}

To assign $P_2$ and $P_3$ to initial or intermediate electronic states, we measured 2PPE spectra of O$_2$/DMSO/Cu(111) as a function of photon energy for four different photon fluences each. The peak positions of $P_2$ and $P_3$ as a function of photon energy are shown in Figure 2(c). As the photon energy is changed, $P_3$ shifts with approximately $2\Delta h\nu$ while $P_2$ shifts with approximately $\Delta h\nu$, meaning that $P_3$ is an initial and $P_2$ is an intermediate state. Based on this, we determine the intermediate state energy of $P_2$ to be $E_{\text{int}}(P_2) = 2.55 \pm 0.03$ eV and the initial state energy of $P_3$ to be $E_{\text{ini}}(P_3) = -0.56 \pm 0.03$ eV with respect to $E_F$.

$E_{\text{int}}(P_2)$ is very similar to the intermediate state energy of the trapped electron of 2.34 eV observed previously\textsuperscript{31} on DMSO/Cu(111) without O$_2$. As in this previous work, the lifetime of $P_2$ is also on the order of several seconds, as expected (cf. Introduction) and shown in the Supplementary Information. We, therefore, assign $P_2$ to a long-lived surface trapped electron ($e_T$) of the O$_2$/DMSO surface. $E_{\text{int}}$ of $e_T$ for the O$_2$/DMSO surface is approximately 200 meV higher in energy than for the pure DMSO surface. This suggests a destabilization of the trapped electron due to the presence of oxygen.

The VBE of $P_3$ is $3.80 \pm 0.05$ eV, determined using equation 4 and the measured O$_2$/DMSO/Cu(111) work function of $\Phi = 3.24 \pm 0.05$ eV. We directly compare this binding energy to the approximate values of the energy of the O$_2$/O$_2^-$/half reaction in DMSO obtained from cyclic voltammetry.\textsuperscript{14,15} Using literature values for the normal hydrogen electrode (NHE) with respect to $E_{\text{vac}}$, as shown in Figure 1(a) and Figure S1.\textsuperscript{14,15} A detailed description of how the electrode potentials are related to the vacuum potential is given in the Supporting Information. CV experiments estimate the VBE of O$_2^-$ between 3.28 and 3.95 eV, i.e. overlapping with the VBE of $P_3$ measured in this work.\textsuperscript{14,15,61}

Moreover, theoretical calculations of O$_2^-$ solvated in DMSO (Supporting Information) determine a VBE between 3.55 and 3.66 eV, in good agreement with our measured $P_3$. Based on the appearance of $P_3$ only on O$_2$-exposed surfaces and similarity with CV measurements and theoretical calculations, we assign $P_3$ to photoemission from O$_2^-$, superoxide. The differences between our measured VBE and those estimated from CV are well within the possible errors due to reference electrode to vac-
uum level calibration and the influence of electrolyte.14,15,41

**Mechanism of O₂ reduction**

Solvent layers effectively screen adsorbed molecular species and electronic states from the metal substrate and often inhibit direct electron transfer through wave function overlap; for reactant molecules adsorbed on insulating solvent surfaces (such as DMSO), a precursor electronic state in the solvent, ideally with a long lifetime, is usually needed for electron transfer leading to anion formation from the reactant molecule.25,26,31 In order to determine whether the short-lived small polaron or the long-lived e₂⁻ is a precursor state to O₂⁻,31 we took 2PPE spectra for O₂⁻-exposed surfaces as a function of DMSO coverage. At low DMSO coverages, where e₂⁻ is not present, but there is a prominent signature of the small polaron,31 the spectroscopic signature of O₂⁻, P₃, is not observed (not shown). Only at sufficiently high DMSO coverages above 2 ML where e₂⁻ is observed does the O₂⁻ signature appear. Therefore, we conclude that e₂⁻ is the precursor state of O₂⁻, as sketched in Figure 2(d), in analogy to previous work on reactivity of surface-trapped electrons at water-ice surfaces.26,37

To determine the mechanism of O₂⁻ formation, we investigated the time-dependence of O₂⁻ formation by measuring 2PPE spectra as a function of surface illumination time. Real-time measurements, instead of ultrafast stroboscopic measurements, are required due to the lifetime of e₂⁻ that exceeds the inverse repetition rate of our laser system, 5 µs. Figure 3(a) shows a representative series of 2PPE spectra of O₂⁻/DMSO/Cu(111) as a function of real-time illumination in false colors. The blue and red arrows indicate the positions of P₂ and P₃ signatures, respectively. (b) Evolution of Φ, P₂ and P₃ intensity as a function of illumination time from the data in (a).

Figure 3: (a) 2PPE spectra of an O₂/DMSO/Cu(111) sample as a function of real-time illumination in false colors. The blue and red arrows indicate the positions of P₂ and P₃ signatures, respectively. (b) Evolution of Φ, P₂ and P₃ intensity as a function of illumination time from the data in (a).

O₂⁻ (P₃, red) extracted by Gaussian fits as in Figure 2(b) and Φ (green) as a function of illumination time. Qualitatively, the delayed rise of P₂ and P₃ is accompanied by a decrease in the sample work function.

In order to explore the origin of these unusual dynamics, we collected similar datasets for different photon energies and fluences, all of which can be found in the Supporting Information. We plot representative data for the fluence-dependent dynamics of e₂⁻, O₂⁻, and Φ for hν = 2.9 eV in Figure 4. As the fluence is increased, the populations of e₂⁻ and O₂⁻ increase, they appear at earlier illumination times, and the early-time drop in the work function occurs faster.
Model of O₂ diffusion in DMSO

We propose that the increase in amplitude of e_T and O₂⁻, the decrease in their appearance time, and the faster Φ decrease observed with increasing photon fluence are all due to diffusion of O₂ into the DMSO layers and reactivity of e_T and O₂ to form O₂⁻. We will now go through this proposed mechanism in detail.

e_T in DMSO are surface-bound electronic states, likely localized at defects within the topmost monolayer. Adsorption of gases on the surface leads to a decrease and/or quenching of photoemission from these states due to dielectric squeezing or blocking of trapped electron binding sites. At the same time, additional adsorbates may alter the surface potential and decrease or enhance the sample work function. The delayed appearance of e_T, accompanied by the work function decrease, suggests that something quenching e_T photoemission intensity and increasing the work function has been removed. As these observations only occur when O₂ is adsorbed, it seems evident that molecular oxygen is the source of both observations.

Both, desorption of O₂ from the surface or diffusion into the DMSO layers - driven by heat supplied by the ultrafast laser system - could be the source of surface O₂ removal and lead to the delayed e_T intensity rise and work function decrease. However, if desorption were the cause, the spectrum after the delayed rise should coincide with a spectrum where O₂ was desorbed by heating the copper substrate above the desorption temperature of O₂ but below the one of DMSO. As shown in Figure S5 in the Supporting Information, this is not the case. Hence, we conclude that diffusion of O₂ into the DMSO layers is the cause for the appearance of e_T (cf. illustration in Figure 3). In addition, decrease in the surface concentration of O₂ through diffusion would also explain the drop in Φ that occurs on the same timescales as e_T and O₂⁻ appearance.

We are able to capture the O₂⁻ photoemission intensity changes with a simple model of O₂ diffusion in DMSO as follows. The diffusion of the O₂ layer into DMSO is approximated using Fick’s law of diffusion in one dimension where all diffusion occurs from the surface into DMSO. In most solids, the diffusion constant D(T) follows an Arrhenius law

\[ D(T) = D_0 \cdot \exp\left(\frac{-E_{\text{diff}}}{k_B T}\right) \]  

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\[ D(T) = D_0 \cdot \exp\left(\frac{-E_{\text{diff}}}{k_B T}\right) \]
where the diffusion depends on an effective temperature, which in our experiments is determined by the photon fluence and is higher than the equilibrium temperature of the sample. We simplify the system into three regions shown graphically in Figure 5(b): the monolayer of adsorbed oxygen $A$ that contributes to the formation of an interfacial dipolar layer and modifies the work function, the region $B$ where near-surface oxygen can still block electron trapping sites, and the reaction region $C$ where the distance of $O_2$ from the surface is small enough that there is sufficient wave function overlap for electron transfer from $e_T$ to $O_2$. Once the $O_2$ molecules have diffused beyond $C$, they cannot be reduced anymore, and the reaction is quenched.

The photoemission signals from $e_T$ and $O_2^-$, $P_3$ and $P_3$, respectively, can both be fit using differential equations that account for the photoexcitation and photoemission processes, diffusion of oxygen and reaction of the trapped electron with $O_2$ forming $O_2^-$. Both are proportional to the incident laser fluence, $F$, and the time-dependent number of accessible sites for $e_T$ formation, $N_{acc}(t)$

$$I_{e_T} \propto F \cdot N_{acc}(t)$$  \hspace{1cm} (6)

$$I_{O_2^-} \propto F \cdot N_{acc}(t) \cdot n_C(t)$$  \hspace{1cm} (7)

where the proportionality constants are determined by the different cross sections for photoexcitation and photoemission, and $n_C(t)$ describes the number of $O_2$ molecules within the region $C$. The density of accessible sites for $e_T$ formation

$$N_{acc}(t) = N_S(t) \cdot \left(1 - \frac{n_B(t)}{n_{O_2}}\right)$$  \hspace{1cm} (8)

depends on the density of electron trapping sites $N_S(t)$, which decreases exponentially with time due to healing of surface defects as observed previously for $e_T$ on crystalline $D_2O$ on Ru(001). The ratio $n_B(t)/n_{O_2}$ describes the fraction of oxygen molecules in the region $B$ that contribute to blocking of trapping sites, i.e. $N_{acc}(t)$ is the fraction of unblocked trapping sites for $e_T$.

The time-dependence of $\Phi$ is fit by considering the number of oxygen molecules $n_A(t)$ that remain in the surface region $A$

$$\Delta\Phi(t) = \mu \cdot n_A(t)$$  \hspace{1cm} (9)

where each surface oxygen molecule contributes a small interfacial dipole $\mu$ that modifies the work function. All of the equations used in the fitting and their detailed explanations can be found in the Supporting Information.

Using this simple diffusion model, we can globally fit the dynamics of $e_T$ and $O_2^-$ across all of the fluences and photon energies. $\Phi$ is also included in the global fit at 2.9 eV, but not at 3.0 and 3.2 eV, as the early-time work function changes at those photon energies occur too quickly to be captured in our experiments, as detailed in the Supporting Information. As shown in Figure 4 and Figure S7, the global fit shows an excellent agreement with the data. From this, we extract the activation energy of diffusion, $E_{diff} = 31 \pm 6$ meV and the temperature-independent diffusion constant of $O_2$ in solid DMSO, $D_0 = (1 \pm 1) \cdot 10^{-20} \text{cm}^2/\text{pulse}$, which can be translated to $D_0 = (1 \pm 1) \cdot 10^{-8} \text{cm}^2/\text{s}$ assuming that each laser pulse heats the surface for approximately 1 ps until the heat is dissipated in the metal substrate through electron-electron and electron-phonon scattering. To our knowledge, this is the first time $D_0$ and $E_{diff}$ of $O_2$ diffusion in solid DMSO has been measured. For $O_2$ diffusion in amorphous solid water, similar values were found.

In the diffusion model, the regions $A$, $B$, and $C$ are dependent upon one another, one region must be set. $A$ is the region where the oxygen interfacial dipole modifies the sample work function, which we set to the van der Waals radius of an oxygen atom, $1.54 \text{ Å}$ as a reasonable minimum distance of the width of the one monolayer of oxygen molecules that forms on the DMSO surface at our deposition temperature of 46 K. Based on this, our global fit yields $B = 4.4 \pm 0.1 \text{ Å}$ and $C = 14.0 \pm 0.4 \text{ Å}$. From these distances we can calculate the DMSO thickness needed to prevent $O_2$ blocking of $e_T$ trapping sites, $B - A$, is $2.8 \pm 0.6 \text{ Å}$, and the
Figure 5: (a) Sketch of sample before illumination, T = 46 K. \( \text{O}_2 \) induces an interfacial dipole and blocks the trapping sites. Hence, no \( e_T \) formation is possible. (b) Sketch of sample under illumination, T > 46 K. \( \text{O}_2 \) diffuses through the adsorbed DMSO. \( A, B \) and \( C \) refer to different regions in DMSO as described in the text.

thickness of DMSO needed to prevent electron transfer to \( \text{O}_2 \), \( x_{\text{react}} = C - A \), is \( 12.4 \pm 0.4 \text{ Å} \). Since the distances \( B, C \), and \( x_{\text{react}} \) are proportional to \( A \), the extracted values from the modelling must also be considered as minimum distances.

We can compare these values with other known distances for DMSO solvation. The radial pair distribution function obtained from X-Ray diffraction and molecular dynamics calculations of solid and liquid DMSO describes how DMSO organizes around other DMSO molecules or around solutes, such as \( \text{O}_2 \) and \( e_T \) studied here. The first coordination shell of liquid DMSO is found between 3-5 Å from other DMSO molecules and solutes. \( 10,47 \) Consistent with this, our experiments found that when \( \text{O}_2 \) was within \( B - A = 2.8 \pm 0.6 \text{ Å} \), from the surface, i.e. within the first solvation shell of surface-trapped electrons \( e_T \), it could suppress the \( e_T \) signal. Furthermore, the end of the third coordination shell of DMSO is approximately 11-12 Å. \( 10,47 \) This value is in good agreement with the reaction quenching distance, \( x_{\text{react}} \), that we determined to be the thickness of DMSO that inhibits electron transfer to oxygen. In other words, on average three solvation shells of DMSO are required to sufficiently damp the electron wave function (i.e. screen the excess electron) to prevent electron transfer from an electronic state such as the \( e_T \) in our experiments. It seems plausible, that similar reaction quenching distances would apply for electron transfer from an electrode surface to \( \text{O}_2 \) or \( \text{O}_2^- \).

The reaction quenching distance for electron transfer in DMSO helps determine the possible mechanisms for the formation of unwanted side-products in metal-air batteries. Simulations by Sergeev et al. \( 10 \) found that \( \text{O}_2^- \) sits between 10-12 Å away from the cathode, far enough away that our experiments suggest DMSO could significantly suppress electron transfer. In contrast, \( \text{LiO}_2 \), which has a high concentration 7 Å from the cathode surface, \( 10 \) is unlikely to be protected from further reduction by DMSO alone because, from our experiments, 7 Å of DMSO are insufficient to prevent electron transfer by screening. Our experiments therefore corroborate the conclusion of Sergeev et al. \( 10 \) that reduction of \( \text{LiO}_2 \) to \( \text{LiO}_2^- \) is a more likely source of electrode passivation in Li-Air batteries than \( \text{O}_2^{2-} \) formation and suggests that the screening of DMSO plays a significant role in this mechanism.

**Conclusion**

In conclusion, we report the formation of \( \text{O}_2^- \) near a DMSO/Cu(111) model battery interface. We were able to directly measure the VBE of \( \text{O}_2^- \) solvated by DMSO is \( 3.80 \pm 0.05 \text{ eV} \) with great accuracy, which may serve as a basis for future calculations on the kinetics of electron transfer at electrode interfaces. We also de-
terminated the energy barrier of oxygen diffusion and diffusion constant in solid DMSO, the reaction quenching distance, $x_{\text{react}}$, of electron transfer in DMSO, which suppresses $O_2$ reduction after approximately 12 Å (approximately three solvation shells of DMSO). Optimizing the electrolyte system to allow for optimal $O_2^-$ formation but suppress side reactions such as $O_2^{2-}$ and $\text{LiO}_2^-$ formation could prevent Li-air battery electrode passivation, a limitation to their repeated use. Our experiments can inform the selection of solvents for battery electrolytes in general by demonstrating the degree of screening required to prevent reduction between diffuse electronic states and small molecular species in solution, an important design criterion.

**Supporting information**

- Conversion between electrochemical potentials and the vacuum level
- Shuttering experiments and decrease in trapped electron lifetime by $O_2$
- Fit of steady-state 2PPE spectrum from $O_2$/DMSO/Cu(111)
- Diffusion vs. desorption of $O_2$
- Derivation of diffusion model

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