Mechanism of oxygen reduction by metallocenes near liquid|liquid interfaces

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ABSTRACT

The mechanism of the oxygen reduction reaction (ORR) at a liquid|liquid interface, employing ferrocene (Fc) derivatives – such as decamethylferrocene (DMFc) – as a lipophilic electron donor along with sulfuric acid as an aqueous proton source, was elucidated through comparison of experimentally obtained cyclic voltammograms (CVs) to simulated CVs generated through COMSOL Multiphysics software which employs the finite element method (FEM). The simulations incorporated a potential dependent proton transfer (i.e. ion transfer, IT) step from the water (w) to organic (o) phases along with two homogeneous reactions (C_1C_2) occurring in the organic phase – an IT-C_1C_2 mechanism. The reaction of DMFc with $H^+(o)$ to form DMFc-hydride (DMFc-H^+) was considered the first step (reaction 1), while reaction of DMFc-H^+ with oxygen to form a peroxyl radical species, HO_2, and DMFc$^+$ was deemed the second step (reaction 2). Subsequent reactions, between HO_2 and either DMFc or H^+, were considered to be fast and irreversible so that 2 was a 'proton-sink', such that further reactions were not included; in this way, the simulation was greatly simplified. The rate of 1, k_{cf}, and 2, k_{chem}, were determined to be 5×10^2 and 1×10^4 L mol^{-1} s^{-1}, respectively, for DMFc as the electron donor. Similarly, the rates of biphasic ORR for 1,1′-dimethylferrocene (DFc) and Fc were considered equivalent in terms of this reaction mechanism; therefore, their rates were determined to be 1×10^2 and 5×10^2 L mol^{-1} s^{-1} for 1 and 2, respectively. The reactive and diffusive layer thicknesses are also discussed.

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1. Introduction

The oxygen reduction reaction (ORR) has been investigated extensively over the past 30 years owing in part to its biological significance [1,2] as well as possible applications in fuel cell technologies [3–11]. In biological systems, oxygen is an electron acceptor in the electron transport chain; this is a key step in cellular respiration that occurs as a trans-membrane process ultimately generating adenosine triphosphate (ATP), the so-called 'energy currency' of the cell, and is housed predominately in the mitochondria [1,2].

The interface between two immiscible electrolytic solutions (ITIES) provides a useful biomimetic utility for the investigation of trans-membrane processes, like ORR [12–17]. The liquid|liquid interface behaves as the junction for charge separation such that the two phases are typically composed of water (w) and an organic

solvent, such as 1,2-dichloroethane (DCE) [12–15]; indeed, this is similar to the behavior exhibited at biological membranes. The potential across the ITIES, called the Galvani potential difference, can be controlled in two ways. First, ions of intermediate solubility can be dissolved in one phase so that their partitioning across the interface generates a potential difference [18,19]. More commonly, the potential can be controlled externally through the use of a potentiostat and electrodes immersed in either phase [12–15]. In this second case, electrochemical measurements can be acquired and are analogous to those obtained through conventional solid–solution, or solid-electrolyte, interfaces. For liquid|liquid electrochemistry, the potentials in the water, ϕ_w, and organic, ϕ_o, phases can be used to control the Galvani potential difference, $\Delta_o^w \phi = \phi_w - \phi_o$, which then becomes the driving force for ion transfer (IT) [12,13].

Biphasic ORR is a key chemical process that has been studied extensively [6,16,20–25] over the past decade by groups such as Kihara et al. [26], Samec et al. [24], Opallo et al. [25], as well as our group [20,22,23,27]. These studies have typically used an

organometallic catalyst, for example porphyrins, along with an electron donor, such as ferrocene (Fc) or decamethylferrocene (DMFc) [23,24]. As demonstrated recently using biscobalt co-facial porphyrins [23], oxygen, through a proposed mechanism studied using density functional theory (DFT), is first bound to the metal center, while acid in the aqueous phase and a Fc derivative in the organic phase provided the protons and electrons, respectively. ORR can also take place without the addition of a catalyst, *i.e.* DMFc and other Fc derivatives can perform ORR, albeit at reduced rates of reaction [21,24]; the mechanism of this reaction was again investigated using DFT calculations where it differed somewhat from the porphyrin catalyzed pathway. Therein, the first step was proton binding to the iron center to form DMFc-hydride [20]. This would subsequently react with dissolved oxygen to form a hydrogen peroxyl radical species that, through further steps, generates the reduction products H_2O_2 or water [20].

The ORR is of considerable importance at both solid-electrolyte [28–30] and liquid|liquid [6,20–26] interfaces owing to its role in possible fuel cell and energy conversion applications. The liquid|liquid interface, between water and an organic solvent, affords several advantages over conventional solid-electrolyte studies in that aqueous acids, such as HCl or H_2SO_4, can be employed while organic acids can be avoided – such as would be necessary for a homogenous organic solvent approach. Additionally, many hydrophobic organometallic catalysts are available, whilst there are very few water-soluble versions that would be required for a single-phase aqueous system. In this way, the two phases provide a convenient method for separating reagents and using existing compounds, while the liquid|liquid interface behaves as a junction for charge separation and is a facile biomimetic [12,13]. With this in mind, biphasic electrochemistry at a large ITIES (centimeter scale) was used to investigate the ORR.

Understanding the mechanism of ORR as well as the kinetics/thermodynamics of such reactions is advantageous as it allows for a modicum of prediction towards possible successful avenues of future research by highlighting significant structural, physicochemical, or reaction conditions. In this way, computational analysis in the form of DFT [21] and finite element analysis, or method (FEM) [31–34], has been used, in tandem with experimental data, to confirm or elucidate proposed reaction pathways. Herein, COMSOL Multiphysics software employing FEM was utilized, with comparison to experimental curve features found in the cyclic voltammetric (CV) experimental data, to further understand ORRs facilitated by DMFc, 1,1′-dimethylferrocene (DFc), and Fc at the w|DCE interface. In this case, it is proposed that DMFc, dissolved in the organic phase, reacts with protons pumped across the interface through three reaction steps to reduce dissolved oxygen (O_2) to hydrogen peroxide (H_2O_2).

2. Simulation

COMSOL Multiphysics version 3.5a, and similar programs utilizing FEM, have been used successfully to simulate a wide variety of processes including surface analysis through Scanning Electrochemical Microscopy [15,35], human neural response to an applied electric field for research into the treatment of Parkinson's disease [36], two-dimensional bipolar electrochemistry [37], solid oxide fuel cells [38], and IT at an ITIES [15,31–34,39,40]. Owing to the incorporation of geometry within the simulation environment, the results take on new meaning beyond those possible with simple numerical computations. Indeed, these types of simulations have been used to predict possible changes in the current–potential response of IT processes brought about by varying geometries of a micro-ITIES held at the tip of a micropipette [31,33,40].

An advantage of COMSOL software is the ability to solve multiple equations, linear or non-linear, simultaneously, such that the diffusion of species through a solution can be coupled with heterogeneous or homogeneous chemical reactions as well as IT. This aspect is of considerable interest in complex, multi-step reactions where it is difficult to differentiate between possible mechanistic pathways. As an example, Kakiuchi et al. [32] used this technique to elucidate the mechanism and kinetics/thermodynamics of interfacial complexation reactions between metal ions dissolved in an aqueous phase and ionophores placed in an ionic liquid; in that report [32], they compared experimentally obtained CVs with simulated ones. Herein, COMSOL is used to evaluate a possible ORR pathway at the w|DCE interface in a similar way, through comparison to features present in CV experimental data.

Fig. 1A illustrates a typical large (centimeter scale) four electrode liquid|liquid electrolytic cell, including a blow-up of the ITIES with the two dimensional simulation geometry marked using a red box. Fig. 1B displays the details of the simulation environment which constituted a radial cross-section of the circular ITIES including the subdomains 1 and 2 used to represent the organic (o) and water (w) phases, respectively. These subdomains are enclosed by ten external boundaries and divided by one internal boundary such that the geometry is a two-dimensional cross-section of the area surrounding the ITIES; in order to reduce computational time further it was recognized that a radial axis-of-symmetry remained, perpendicular to the interface and the simulation environment was reduced by half. A detailed description of the simulation boundary conditions have been given in the caption of Fig. 1; however, boundary 5 is significant as it was the w|o interface and was used to describe the flux of species – its boundary condition was set as 'flux'. IT at boundary 5, of the form:

$$i_w^{z_i} \rightleftharpoons i_o^{z_i} \tag{1}$$

where ion i of charge z_i transfers from w to o, was approximated using Butler–Volmer kinetics which describe the forward (k_f) and reverse (k_b) rate constants through the following, facile potential dependent equations:

$$k_f = k^0 \exp\left[-\alpha f(\Delta_o^w \phi - \Delta_o^w \phi^{0'})\right] \tag{2}$$

$$k_b = k^0 \exp\left[(1-\alpha)f(\Delta_o^w \phi - \Delta_o^w \phi^{0'})\right] \tag{3}$$

In Eqs. (2) and (3), k^0 is the standard rate constant, α is the transfer coefficient (assumed to be 0.5 unless otherwise stated), and $f_i = z_iF/RT$; such that F, R, and T are Faraday's constant, the universal gas constant, and temperature in Kelvin, respectively. $\Delta_o^w \phi$ was applied in the simulation through the use of a triangular waveform [40] implemented directly into Eqs. (2) and (3); thus, generating a potential sweep with time analogous to the scanning programs found in CV. Finally, $\Delta_o^w \phi^{0'}$ is the formal IT potential, which is a constant and property individual to each species and biphasic system.

Mass transport within each phase was handled using Fick's laws of diffusion and this is given below for the cylindrical coordinate system employed herein:

$$\frac{\partial c_{i,w}(r,z,t)}{\partial t} = D_{i,w}\left(\frac{\partial^2 c_{i,w}(r,z,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c_{i,w}(r,z,t)}{\partial r} + \frac{\partial^2 c_{i,w}(r,z,t)}{\partial z^2}\right)$$
$$= D_{i,w}\nabla c_{i,w}(r,z,t) \tag{4}$$

where $D_{i,w}$ and $c_{i,w}$ are the diffusion coefficient and concentration of species i in phase w and ∇ is the gradient operator; an analogous equation can be written for species in the organic phase.

The current response with respect to charge transfer across the ITIES at boundary 5, was calculated as the integral of the flux of ions at the interface as given below: