



# Electrochemical oxygen reduction at soft interfaces catalyzed by the transfer of hydrated lithium cations



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## ABSTRACT

The oxygen reduction reaction by decamethylferrocene (DMFc), triggered by hydrophilic metallic cations behaving as Lewis acids towards water molecules in a homogeneous organic phase reaction, was investigated using cyclic voltammetry at the water|1,2-dichloroethane (w|DCE) interface. Simulated CVs, prepared through a facile 1-dimensional geometry in COMSOL Multi-physics software and incorporating interfacial and homogeneous reactions, were compared to experimental ones in order to elucidate the kinetics, thermodynamics, and viability of the proposed mechanism. The predominant O<sub>2</sub> reduction reactions were proposed to occur in bulk organic phase, or in the vicinity of the w|DCE interface; six organic phase reactions were put forward. The first step was hydrolysis made possible through polarization of the O–H bond of water molecules available in the cations hydration shell. The metal ion behaves as a Lewis acid coordinating to the oxygen and weakening the O–H bond, making the proton more acidic, thereby facilitating attack by decamethylferrocene (DMFc) to form DMFc–H<sup>+</sup>. DMFc–H<sup>+</sup> then participates in dioxygen reduction, generating the O<sub>2</sub>H<sup>•</sup> radical species and DMFc<sup>+</sup>. Afterwards, the radical oxidizes another equivalent of DMFc to produce O<sub>2</sub>H<sup>–</sup>, that can then abstract a proton from the metal ions hydration sphere to generate hydrogen peroxide. The disproportionation of O<sub>2</sub>H<sup>–</sup> and the ion-pair formation of Li<sup>+</sup> and OH<sup>–</sup> make up the other two reactions. The CV analysis was based on two curve features; the DMFc<sup>+</sup> transfer wave and the positive limit of the polarizable potential window – the edge of scan potential profile – including the metal ion return peak. The goal of this article is to determine the kinetic/thermodynamic aspects of this mechanism from the experimental electrochemical data.

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## 1. Introduction

The oxygen reduction reaction (ORR) at metal surfaces [1–4], in solution [2,5–8], and in biological systems is of considerable importance as it impacts solid electrode performance and is an integral reaction for fuel cells and artificial photosynthesis [9]. In the case of hydrogen fuel cells, poor O<sub>2</sub> reduction kinetics elicit appreciable overpotentials that greatly limit the power outputs [2] of the device stimulating interest in mechanistic and kinetic characterization of this reaction. To that end, the ORR has been extensively studied in organic and aqueous systems, while recently expanding to include novel solvents such as ionic liquids [10,11]. At the same time, a great deal of research has been directed towards the development of new, cheaper catalysts such as

metal-porphyrins [12–14]. In the past 10 years non-heme iron(IV)-oxo catalysts have come under attention [15–17], and it has been demonstrated that polymer based cathodes incorporating these catalysts were comparable to traditional Pt cathodes.

Simultaneously, oxygen reduction has been characterized at the interface between two immiscible electrolytic solutions (ITIES) [5–7,18–25], often between water and an organic solvent (e.g., 1,2-dichloroethane, DCE). Electrochemistry at an ITIES has several advantages over conventionally solid/liquid methods. For example, the liquid|liquid interface is intrinsically defect free; therefore, it does not require the extensive polishing associated with solid electrodes. Additionally, the water and organic phases can be treated as a convenient means for product or reagent separation – in some cases facilitating charge separation – while early studies focused on evaluating porphyrin-based catalysts [18,26].

Regardless of which system is employed – solid/electrolyte [2,3,14,16], liquid|liquid [5,8,13,18–21,23–25,27,28], or homogeneous [7,8,12,22] – or which catalyst is used, an electrode or an electron donor, which can be sacrificial, is typically required. Here,

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decamethylferrocene (DMFc), 1,1'-dimethylferrocene (DFc), or ferrocene (Fc) are used as organic electron donors. Samec et al. reported that significant changes in the rate of the ORR reaction could take place depending on which electron donor was utilized [28]. They also reported a strong inhibition of a cobalt-porphyrin catalyzed ORR through a proposed coordination of H<sub>2</sub>O to the cobalt center in a homogeneous organic phase experiment [5]. Additionally, it has been discovered that sufficiently strong electron donors, like many ferrocene derivatives, could perform O<sub>2</sub> reduction independently in the absence of a catalyst, when protons are available, albeit much slower [6,20,22,24,27]. A mechanism was then proposed based on spectroscopic and kinetic/thermodynamic evidence for the DMFc, water|DCE (w|DCE) case [6,20,22]. First, the proton undergoes ion transfer from water (w) to organic (o) phase where it then binds to the metal center of DMFc forming the DMFc-hydride (DMFc-H<sup>+</sup>) [6,20,22]. DMFc-H<sup>+</sup> subsequently reacts with dissolved O<sub>2</sub> to form DMFc<sup>+</sup> and the hydrogen peroxyl radical, O<sub>2</sub>H<sup>•</sup> [6,20,22]. O<sub>2</sub>H<sup>•</sup> can oxidize one equivalent of DMFc to form DMFc<sup>+</sup> and O<sub>2</sub>H<sup>-</sup>, which can then either become protonated to form H<sub>2</sub>O<sub>2</sub> or disproportionate to form dioxygen and two equivalents of OH<sup>-</sup>.

This is one possible O<sub>2</sub> reduction mechanism, as recently outlined by Girault et al. [6]; however, a novel mechanism, utilizing alkali metals in the absence of an acid, has recently been evidenced [7], in which water – dissolved in the organic phase – becomes the proton source in a Lewis acid catalyzed reaction. Through this pathway [7], the alkali, or other metal ion, transfers from the aqueous to organic phase – either into a hydration pocket, as has been shown [29], or with some of its hydration sphere intact. The metal ion, coordinating to the oxygen of the surrounding H<sub>2</sub>O molecules, weakens the O–H bonds within the hydration sphere and facilitates the abstraction of a proton by DMFc to form DMFc-H<sup>+</sup> [7]. In this way, the metal ion behaves as a Lewis acid with the subsequent proposed mechanistic steps mirroring those of the previous acid catalyzed pathway.

Metals, particularly transition metals, behaving as Lewis acids have been used to catalyze synthetic reactions with significant architectures [30] or stereochemistry for decades [31]. Fukuzumi et al. have recently demonstrated that the reactivity of the Fe(IV)=O moiety within the non-heme iron(IV)-oxo catalysts – when used for C-bond cleavage – can be enhanced through the presence of Lewis acids such as triflic acid or scandium(III) triflate [32]. While this Lewis acid behaviour is generally well known, its incorporation into DMFc mediated O<sub>2</sub> reduction is novel [7].

The goal of the present work is to consolidate the electrochemical evidence acquired at biphasic (in this case w|DCE) systems obtained through cyclic voltammetry (CV), with previous spectroscopic (mass spectroscopy, UV/Vis, etc.) observations [7] and elucidate the kinetics/thermodynamics of Lewis acid catalyzed O<sub>2</sub> reduction at liquid|liquid interfaces. To achieve this, COMSOL Multi-physics was employed utilizing a facile 1-dimensional geometry of the w|DCE interface (millimeter scale), to generate simulated CVs. By altering the rates of the different reaction steps, recording the resultant changes in the simulated CV, and then comparing them to the experimental ones, the mechanism proposed herein was investigated.

## 2. Simulations

Simulation software, like COMSOL Multi-physics, which employs the finite element method, has been used to evaluate a broad spectrum of phenomenon including nanocrystalline phase change memory cells [33], the thickness of methanol fuel cell cathode catalyst layers [34], hydrogen storage tanks [35], nuclear fuel bundles [36], and a host of electrochemical phenomenon [37–39];

the latter has been subject to a recent mini-review concerning electrochemical analysis [40]. Herein, this versatile software was used to explore the mechanism and kinetics of O<sub>2</sub> reduction in water|organic solvent (w|o), biphasic systems. The model, comprised of a facile 1-dimensional geometry depicted in Fig. 1, contained two subdomains to represent either phase and three boundaries. The boundaries at the terminal ends of the geometry in Fig. 1 were given the designation 'concentration' in the software, which is used to describe the bulk concentration of species unaffected during the time scale of the experiment. Mass transport, for the fully supported electrolyte solution, was described within each phase using Fick's laws as per the following equation,

$$\frac{\partial c_{i,w}(x,t)}{\partial t} = D_{i,w} \nabla c_{i,w}(x,t) = D_{i,w} \left( \frac{\partial^2 c_{i,w}(x,t)}{\partial^2 x} \right) \quad (\text{i})$$

for a 1-dimensional system, such that  $c_{i,w}$  and  $D_{i,w}$  are the concentration and diffusion coefficient of species  $i$  in water (w); an analogous equation can be written for the organic (o) phase. A model incorporating the Nernst–Planck series of equations describing mass transport, which take into account diffusion along with migration, was considered. However, migration was deemed a small contributor at experimental, electrolyte concentrations to the overall current density; furthermore, the complexity of programming such a system was found to be prohibitive. Therefore a more facile simulation employing only Fick's laws was considered moving forward.

Potential dependent ion transfer (IT) across the central boundary (Fig. 1) of an ion, with a charge  $z_i$ , can be written as:

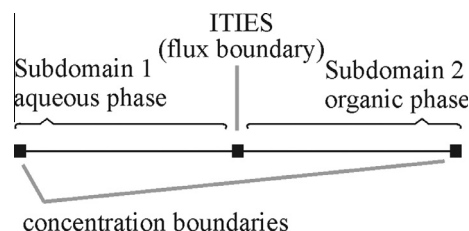
$$I_w^z = I_o^z \quad (\text{ii})$$

IT was controlled using Butler–Volmer kinetics described by the forward and reverse,  $k_f$  and  $k_b$ , rate constants, respectively, through the following:

$$k_f = k^o \exp(-\alpha f (\Delta_o^w \phi - \Delta_o^w \phi^{or})) \quad (\text{iii})$$

$$k_b = k^o \exp((1 - \alpha) f (\Delta_o^w \phi - \Delta_o^w \phi^{or})) \quad (\text{iv})$$

where  $k^o$  is the standard rate constant (a value of 1 cm s<sup>-1</sup> was used unless otherwise noted for fully reversible IT),  $\alpha$  is the transfer coefficient (0.5 was used throughout), and  $f$  is  $F/RT$ , where  $F$  is Faraday's constant,  $R$  is the universal gas constant, and  $T$  is temperature.  $\Delta_o^w \phi$  is the Galvani potential difference across the interface,  $\phi_w - \phi_o = \Delta_o^w \phi$ , and was approximated using a triangular waveform [39,41] in order to mirror the CV experiments. A formal IT potential,  $\Delta_o^w \phi_i^{or}$ , of 0.696 V, described for lithium cations [42] at the w|DCE interface, was used throughout unless otherwise stated.



**Fig. 1.** The 1-dimensional simulation geometry (thin black line) with three boundaries (squares) as drawn in COMSOL Multi-physics software. The geometry was split into subdomains 1 and 2 representing the aqueous and organic phases, respectively, within which mass transport was governed by Fick's laws of diffusion. The outer boundaries were given the designation 'concentration' in the software, representing the bulk solution beyond which point the solution concentration profile is not expected to change on the time scale of the experiment. The interface between two immiscible electrolytic solutions (ITIES), shown at center, was given the boundary condition 'flux', such that species could cross the interface either through ascribed partition coefficients or through potential dependent ion transfer described by Butler–Volmer kinetics.

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