



The electrochemical reduction kinetics of oxygen in dimethylsulfoxide

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ABSTRACT

The quasi-reversible one-electron reduction of oxygen in dimethylsulfoxide is reported for a range of electrode materials (C, Pt, Pd, and Au) and temperatures (293–343 K). Modelling was undertaken using Butler-Volmer and symmetric Marcus-Hush methods, with the former found to provide more reproducible results for this system, in agreement with previous reports of quasi-reversible systems. The reorganisation energy for the reaction was found to be ca. 1.0 eV, and the reaction confirmed to be predominantly outer-sphere. The observed standard electrochemical rate constant (k_0) is ca. 5.7 times faster for C electrodes than Pt, despite having a lower electronic density of states.

1. Introduction

The oxygen reduction reaction (ORR) is of fundamental importance to many electrochemical energy applications, for example metal-air batteries and fuel cells. In the case of reactive metal-air (or oxygen) batteries, aprotic solvents are commonplace and dimethyl sulfoxide (DMSO) is widely used [1,2]. A detailed understanding of the kinetics of oxygen reduction in DMSO is therefore desirable, including any effects of electrode material on the kinetics. It is anticipated that such studies may help inform aspects of (metal-air) battery and fuel cell design.

Furthermore, the complexity of the aqueous ORR has led some workers to seek proxy systems, especially for theoretical studies where aprotic solvents provide the simplest ORR, with quasi-reversible one electron transfer (Eq. (1)). DMSO is an interesting experimental system due to its miscibility with water and potential for mixed-solvent ORR studies.



For the one-step electron reduction of oxygen the kinetics can be most easily described using either the Butler-Volmer or Marcus-Hush approaches [3]. The ubiquitous Butler-Volmer model relates the reductive and oxidative electron transfer rate constants for Eq. (1), to the overpotential ($E - E_f^0$) via a transfer coefficient (α or β) and a standard heterogeneous electrochemical rate constant (k_0):

$$k_{red} = k_0 \exp \left[\frac{-\alpha F (E - E_f^0)}{RT} \right] \quad (2)$$

and

$$k_{ox} = k_0 \exp \left[\frac{+\beta F (E - E_f^0)}{RT} \right] \quad (3)$$

where F is Faraday's constant, R the universal gas constant and T the absolute temperature.

The symmetric Marcus-Hush (SMH) model has become increasingly used to gain insight into the physical process at the molecular level [4–8]; in the case of a diffusional outer-sphere electron transfer process, the SMH defines the standard electrochemical rate constant, k_0 , as:

$$k_0 = \frac{2\pi^{3/2}\rho |H_{DA}|^2}{\beta h \Lambda^{1/2}} \exp \left(-\frac{\Lambda}{4} \right) I(0, \Lambda) \quad (4)$$

where ρ is the density of electronic states of the electrode material, H_{DA} is the electronic coupling matrix between the electrode and electroactive species (donor and acceptor) at their closest distance of approach, β in this context is the electronic coupling attenuation coefficient (linked to H_{DA}), and h is Planck's constant [7,8]. The parameters Λ and $I(0, \Lambda)$ are given by:

$$\Lambda = \frac{F}{RT} \lambda \quad (5)$$

and

$$I(\theta, \Lambda) = \int_{-\infty}^{\infty} \frac{\exp \left\{ -\frac{(\epsilon - \theta)^2}{4\Lambda} \right\}}{2 \cosh \left(\frac{\epsilon}{2} \right)} d\epsilon \quad (6)$$

where

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$$\theta = \frac{F}{RT}(E - E_f^0) \quad (7)$$

and where λ is the Marcus reorganisation energy and ε is an electronic state, with k_0 defined at $\theta = 0$. [7,8]

The one-electron reduction of dioxygen to superoxide is usually treated as an outer-sphere electron transfer, regardless of electrode material or solvent [9]. Here we report a study of the electro-reduction kinetics of oxygen dissolved in DMSO, varying electrode material and temperature to determine the reorganisation energy of Eq. (1) and the source of material-effects on the kinetics in the absence of a classical surface-analyte bond (inner sphere) interaction.

2. Experimental

The following chemicals and gases were obtained commercially and used without further purification: potassium chloride (Sigma Aldrich, > 99%), hexaammineruthenium (III) chloride (Sigma Aldrich, > 99%), tetra-*n*-butylammonium perchlorate, (TBAP, Fluka, < 99%), potassium nitrate (Sigma Aldrich > 99.99%), dimethyl sulfoxide (DMSO, Sigma Aldrich > 99%), nitrogen (oxygen-free, BOC Gases plc), and oxygen (N5 grade, BOC Gases plc). DMSO was stored over molecular sieves prior to use.

All solutions were made with sufficient inert electrolyte to be fully supported and thoroughly purged with either nitrogen or oxygen as appropriate. In addition, the aqueous solutions used for electrochemical calibration of electrodes were made with ultrapure water of resistivity not < 18.2 M Ω cm (milliQ, Millipore). Variable temperature experiments were conducted by heating the solution in a thermostatted water bath (with the reference electrode within the thermostatted reaction cell), with temperature measurements confirmed via a mercury thermometer.

Electrochemical measurements were made using a three electrode arrangement in a faraday cage, controlled by a PGStat128N potentiostat (Metrohm-Autolab BV, Utrecht, NL). A saturated Ag/AgCl leakless reference electrode and bright platinum mesh counter electrode were used. The working microelectrodes used were carbon, platinum (both from BASI Inc.), platinum and palladium (both fabricated in-house), and were all of microwire-in-glass construction. The radii of the working microelectrodes employed were confirmed via steady state linear sweep voltammetry of the reduction of 1 mM hexaammineruthenium(III) chloride in 0.1 M KNO₃, and were calculated to be as follows: C 4.8 μ m, Pt 5.0 μ m, Pd 12.2 μ m, and Au 10.9 μ m. A Pt macroelectrode (radius 2.5 mm) was used for diffusion coefficient measurements.

3. Results & discussion

First, linear sweep voltammetry (LSV) was used to determine the diffusion coefficients and saturated concentration of dioxygen in DMSO at different temperatures using a Pt microelectrode and macroelectrode. The measured steady-state limiting and peak currents (I_{lim} and I_p respectively) from these scans were compared to determine the diffusion coefficient, D , according to Eqs. (1)–(3) for a 1e⁻ transfer [3].

$$I_{lim} = 4FCDr_d \quad (8)$$

$$I_p = (2.99 \times 10^5)\pi R^2 C (\alpha D\nu)^{1/2} \quad (9)$$

Therefore

$$\frac{I_{lim}}{I_p} = 0.411 \left(\frac{r_d}{R^2} \right) \left(\frac{D}{\alpha\nu} \right)^{1/2} \quad (10)$$

where F is the Faraday constant, r_d is the microdisk radius, R is the macrodisk radius, α is the transfer coefficient and ν is the voltage scan rate (here 25 mV s⁻¹). The value of α was determined from a Tafel plot of the Pt macroelectrode LSV and confirmed through modelling of the

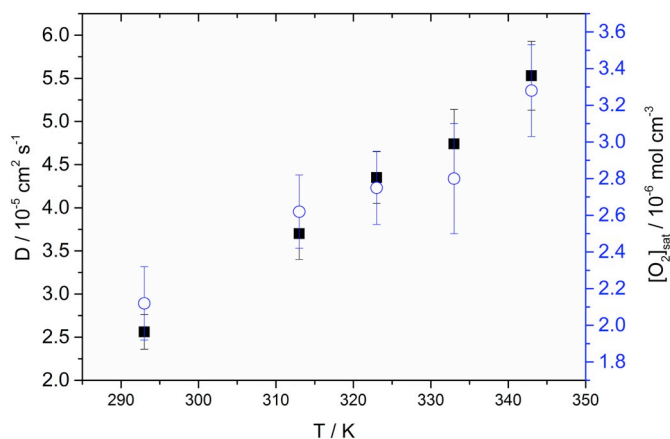


Fig. 1. The variation of diffusion coefficient of oxygen (■) and $[O_2]_{sat}$ (○) with temperature in a solution of 0.1 M TBAP in DMSO.

Pt microelectrode LSV to be 0.36. The values of D and $[O_2]_{sat}$ over the temperature range 293–343 K are shown in Fig. 1 below.

These results are consistent with literature values for $[O_2]_{sat}$ at 298 K of 2.1 mM [10]. Literature reports for diffusion coefficients across that temperature range from 2.2×10^{-5} to 7.49×10^{-5} cm² s⁻¹ [10–13]. An Arrhenius-type plot of the data in Fig. 1 yields a gradient of 1.53×10^3 K⁻¹ ($R^2 = 0.991$), corresponding to an activation energy for diffusion of ca. 12.7 kJ mol⁻¹.

Next, the LSV for the reduction of oxygen in DMSO was recorded at: (i) carbon, platinum, gold, and palladium microelectrodes at 293 K, and (ii) carbon and platinum microelectrodes at a range of temperatures between 293 K and 343 K.

The voltammetry was then modelled via commercial software (DigiElch™) which is capable of modelling experimental data via either Butler-Volmer, or symmetric Marcus-Hush algorithms. Simulations were performed using both methods for comparison in order to determine the optimal model to use [7,8], and these are detailed in the Supporting Information along with a selection of ‘best-fits’ to experimental data.

In brief it was found that the SMH model gave inconsistent results, which we ascribe to the known difficulties in fitting quasi-reversible and irreversible voltammetry to the symmetric MH model [8,14–17]. We therefore proceeded with the Butler-Volmer simulation to extract values for the standard electrochemical rate constant (k_0), transfer coefficient (α), and formal potential (E_f^0). Table 1 shows the fitted parameters – the variation in formal potential is ascribed to ‘drift’ on the aqueous reference electrode.

Fig. 2(a) illustrates the variation in k_0 with electrode material at

Table 1

Fitted BV parameters for variable temperature linear sweep voltammetry of oxygen reduction at 4 different electrode materials.

T/K	Platinum			Carbon		
	$k_0/10^{-3}$ cm s ⁻¹	α	E_f^0/V	$k_0/10^{-2}$ cm s ⁻¹	α	E_f^0/V
293	7.5	0.36	-0.520	4.3	0.41	-0.495
303	10.0	0.34	-0.460	6.2	0.42	-0.366
313	14.0	0.37	-0.340	8.0	0.42	-0.270
323	20.0	0.33	-0.365	9.9	0.39	-0.270
333	-	-	-	13.5	0.39	-0.315
343	30.0	0.44	-0.360	17.5	0.36	-0.330
	Palladium			Gold		
	$k_0/10^{-3}$ cm s ⁻¹	α	E_f^0/V	$k_0/10^{-3}$ cm s ⁻¹	α	E_f^0/V
293	4.0	0.35	-0.755	6.0	0.39	-0.500

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