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Electrochemical Promotion of Catalysis

II: The Role of a Stable Spillover Species and Prediction of Reaction Rate Modification

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A simple model to describe the reversible electrochemical promotion of supported metal catalysts has been formulated. This model is derived from first principles and allows for the presence of two forms of catalyst surface oxygen, one ionic and one neutral. Both forms of surface oxygen are able to undergo charge-transfer reactions with the solid–electrolyte ion-conducting support. The ionic oxygen is assumed to be the only ion present with a significant surface coverage and, as such, dictates the properties of the catalyst surface double layer. Using the adsorption isotherm for oxygen ions it is easy to show that in the presence of significant lateral interactions the change in catalyst surface potential must be less than the overpotential applied to the catalyst/support interface. By considering a simple reaction mechanism that involves a charged transition state and accounting for the effect of long-range electrostatic interactions it is possible to express reaction rates as a function of applied overpotential. It is shown that under certain conditions reaction rates are predicted to increase on application of both negative and positive overpotentials (for both positively charged and negatively charged transition states), in agreement with some experimental studies, as a result of electron donation and acceptance from both the metal catalyst and the surface O/O^{2-} redox couple. In addition the enhancement factor (the ratio of change in reaction rate to electrochemical oxygen flux) is shown to depend upon the selectivity for oxygen ion formation from charge-transfer and adsorption processes. © 2001 Academic Press

1. INTRODUCTION

It has been shown by Vayenas and co-workers that when an active catalyst, in the form of an electrode in a solid–electrolyte electrochemical cell, has ions supplied to it or removed from it, there can be a dramatic change in the activity of the catalyst. Such an effect has been termed the non-Faradaic electrochemical modification of catalytic activity (NEMCA). Electrochemical promotion, or NEMCA, has been observed for over 50 catalytic reactions (a number of reviews exist (1, 3, 4)) performed over a number of metal catalysts with differing supports (5) including oxygen-ion conductors (6–11), sodium-ion conductors (12), proton conductors (13–15), and fluorine conductors (16). Electrochemical promotion has also been observed in the case of a titania mixed ionic-conducting and electronic-conducting support (2). The effect has been explained in terms of a modification of the work function of the electrode catalyst as a result of changes in the electrode overpotential; these changes in the work function have been confirmed by the use of a Kelvin probe (9). It has been found that (9)

$$\eta = \Delta\Phi \qquad [1]$$

where η is the applied overpotential and $\Delta\Phi$ is the change in electron extraction potential of the catalyst and any imposed overpotential is reflected by a change in the macroscopically determined work function (determined with a Kelvin probe). It has been postulated that the work function of the catalyst is changed by an electrochemically induced oxygen species, much less reactive and more ionic than chemisorbed oxygen, which spills over the catalyst surface. Other workers (17–20) have found that any electron extraction potential change may be less than the applied overpotential possibly due to finite reactivities and diffusivities of the spillover species and, in general,

$$\eta = \Delta\Phi + \Delta\Psi, \qquad [2]$$

where $\Delta\Psi$ is the change in outer potential.

The induced change in work function modifies the kinetic behaviour of the catalyst and, in general, the new reaction, R, can be related to the overpotential by an equation of the form (e.g., 1)

$$\ln\frac{R}{R^0} = \alpha\frac{e(\Delta\Phi - \Delta\Phi^*)}{kT}, \qquad [3]$$

where k is the Boltzmann constant, R^0 is the open-circuit reaction rate, e is the charge on an electron, and α and $\Delta\Phi^*$ are empirically determined constants. Interestingly a number of empirical studies (methanol oxidation

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over yttria-stabilized-zirconia-supported platinum (e.g., 1) carbon monoxide oxidation over both YSZ-supported platinum and YSZ-supported silver (e.g., 1), methane oxidation over YSZ-supported platinum (e.g., 1), and ethylene oxidation over titania-supported platinum (2) and YSZ-supported silver (e.g., 1)) have shown that α can be positive for positive overpotentials and negative for negative overpotentials resulting in reaction rate increases for both polarities.

Vayenas *et al.* (e.g., 1) have compared the change in reaction rate to the flux of ions needed to cause the change. For an oxygen-ion conductor,

$$\Lambda = \frac{2F\Delta R}{I}, \qquad [4]$$

where Λ is known as the enhancement factor (which is dimensionless), ΔR is the change in reaction rate, and $I/2F$ is the flux of ionic oxygen. (It should be noted that Vayenas *et al.* do not use area specific reaction rates and current densities and therefore Λ would be expected to be a function of electrode morphology as well as operating conditions.) Furthermore, the enhancement factor can be estimated from the open-circuit reaction rate and the exchange current (e.g., 1),

$$\Lambda = \frac{2FR^0}{I_0}. \qquad [5]$$

In Part I of this work (21) a metal catalyst in the form of an electrode supported on an oxygen-ion-conducting solid–electrolyte support within a gradientless reactor was considered. The reactions involving oxygen were described by a simple reaction network (see Fig. 1). Only two forms of catalyst surface oxygen, neutral oxygen and doubly charged ionic oxygen, were considered to have significant coverages (the coverages of all other ions was assumed to be insignificant). Reactions 1 and 2 are charge-transfer reactions involving neutral adsorbed oxygen and adsorbed ionic oxygen, respectively. Adsorbed ionic oxygen can decompose through Reaction 3 to form neutral adsorbed oxygen and electrons associated with the bulk of the metal. Reaction 4 represents oxygen adsorption and desorption. Reactions 5 and 6 involve the removal of surface oxygen and surface ionic oxygen respectively by reaction with a reducing gas. Reaction 6 is considered to be slow. In Part I (21) it was shown that the activation overpotentials for the individual reactions, η_i, are related to the electrode overpotential, η, through the following relationships in the case of fast surface and gas-phase diffusion of species:

$$e\eta_1 = e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O}} \qquad [6]$$

$$e\eta_2 = e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}} - e\Delta\chi - e\Delta V_{\mathrm{lat,O}^{2-}} \qquad [7]$$

$$e\eta_3 = e\Delta\chi + e\Delta V_{\mathrm{lat,O}^{2-}} + \frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}} - \frac{1}{2}\Delta\mu_{\mathrm{O}} \qquad [8]$$

$$e\eta_{4/5} = \frac{1}{2}\Delta\mu_{\mathrm{O}}, \qquad [9]$$

where χ is the catalyst surface potential, $V_{\mathrm{lat,O}^{2-}}$ is the lateral dipole–dipole interaction potential between adsorbed oxygen ions, μ_{O} is the chemical potential of adsorbed neutral oxygen, and $\mu_{\mathrm{O}^{2-}}$ is the chemical potential of adsorbed oxygen ions.

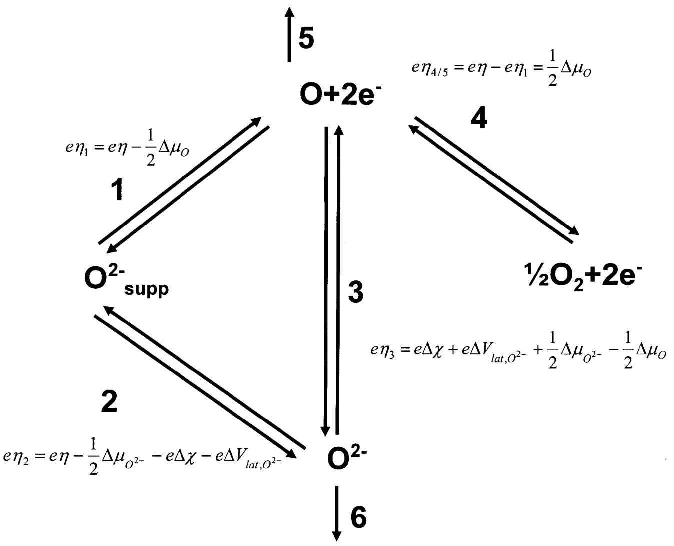

FIG. 1. Reaction network for electrochemical oxygen supply to a metal surface showing driving forces for individual reactions.

In this paper, Part II, we will again confine ourselves to the situation of a metal catalyst supported on an oxygen-ion-conducting solid electrolyte within a gradientless reactor. Only two forms of surface oxygen are present, one being ionic; there are negligible coverages of all other ions in so far as double-layer effects are concerned and there is fast surface and gas-phase diffusion of all species. Furthermore, we will consider the case of a stable ionic oxygen spillover species. Reactions 3 and 6 are slow and therefore Reaction 2 can be considered to be fast. At steady state Reaction 2 will be at equilibrium,

$$\eta_2 = 0 \qquad [10]$$

Therefore, as a result of this equilibrium between support and catalyst surface ionic oxygen, the actual nature of the reaction network is unimportant and no explicit reference will be made to it (except for within the discussion on the enhancement factor where the network proposed in Part I (21) will be used for illustration). We will start by investigating the relationship between change in surface potential and applied overpotential. The characteristics associated with reaction rate modification will then be predicted by using transition state theory and considering the role of long-range electrostatic interactions in the absence of any short-range effects. Finally the physical origin of the enhancement factor will be investigated. (It should be noted that Imbihl *et al.* (22) have recently investigated reaction rate modification and the physical meaning of the enhancement factor using a less-detailed phenomenological analysis.) In common with Part I we will confine ourselves to the consideration of oxygen-ion spillover. However, the approach adopted could equally be applied to other systems.

2. SURFACE POTENTIAL AS A FUNCTION OF OVERPOTENTIAL

A consequence of spillover ionic oxygen being relatively stable and involved in fast charge-transfer and diffusive processes is that the electrochemical potential of oxygen ions in the support must remain equal to the electrochemical potential of oxygen ions at any point on the metal surface at steady state. As the electrochemical potential of oxygen ions in the support is uniform (high ionic conductivity) and constant (fixed-potential reference electrode), the electrochemical potential of adsorbed oxygen ions is always equal to its unpolarised value during steady operation,

$$\bar{\mu}_{\mathrm{O}^{2-}} = \bar{\mu}^0_{\mathrm{O}^{2-}}, \qquad [11]$$

where the superscript 0 is used to signify the initial unpolarised value. Therefore,

$$\Delta\bar{\mu}_{\mathrm{O}^{2-}} = 0. \qquad [12]$$

However, the electrochemical potential can be related to the chemical potential,

$$\frac{1}{2}\bar{\mu}_{\mathrm{O}^{2-}} = \frac{1}{2}\bar{\mu}_{\mathrm{O}^{2-}} - e\phi_{\mathrm{O}^{2-}}. \qquad [13]$$

For the case of oxygen ions being the only ions present in significant amounts, we may express the potential of electrons associated with the oxygen ions, $\phi_{\mathrm{O}^{2-}}$, in terms of metal potential, ϕ, surface potential and lateral dipole–dipole interaction potential,

$$\phi_{\mathrm{O}^{2-}} = \phi - \chi - V_{\mathrm{lat,O}^{2-}}, \qquad [14]$$

and

$$\frac{1}{2}\bar{\mu}_{\mathrm{O}^{2-}} = \frac{1}{2}\mu_{\mathrm{O}^{2-}} + e\chi + eV_{\mathrm{lat,O}^{2-}} - e\phi. \qquad [15]$$

Using Eqs. [12] and [15],

$$e\eta = \frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}} + e\Delta\chi + e\Delta V_{\mathrm{lat,O}^{2-}}, \qquad [16]$$

recovering Eq. [7] with η_2 equal to zero, as

$$\eta = \Delta\phi = \phi - \phi^0.$$

In Part I of this work (21) the oxygen-ion adsorption isotherm was derived, i.e., expressions for the change in chemical potential of oxygen ions, the change in surface potential and the change in lateral interaction potential were all obtained,

$$\Delta\mu_{\mathrm{O}^{2-}} = kT \ln \frac{\theta_{\mathrm{O}^{2-}}}{\theta_*}\frac{\theta^0_*}{\theta^0_{\mathrm{O}^{2-}}} \qquad [17]$$

$$\Delta\chi = \frac{N\mu}{\varepsilon_0}\left(\theta_{\mathrm{O}^{2-}} - \theta^0_{\mathrm{O}^{2-}}\right) \qquad [18]$$

$$\Delta V_{\mathrm{lat,O}^{2-}} = \frac{N\mu}{\varepsilon_0}\frac{\pi\sqrt{3}}{16}\frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}}\left(\theta^{3/2}_{\mathrm{O}^{2-}} - \theta^{0\,3/2}_{\mathrm{O}^{2-}}\right), \qquad [19]$$

where θ_* and $\theta_{\mathrm{O}^{2-}}$ refer to the coverages of vacant sites and oxygen ions, N is the site density, μ is the dipole moment of the oxygen ion, ε_0 is the vacuum permittivity, $a_{\mathrm{O}^{2-}}$ is the dipole separation distance for the oxygen ion, and $r_{\mathrm{O}^{2-}}$ is the effective ionic radius of the oxygen ion.

Substituting for the change in chemical potential of oxygen ions, the change in surface potential and the change in lateral dipole-dipole interaction potential in terms of oxygen-ion coverage using Eqs. [17], [18], and [19], respectively into Eq. [16] we obtain

$$e\eta = \frac{kT}{2}\ln\frac{\theta_{\mathrm{O}^{2-}}}{\theta_*}\frac{\theta^0_*}{\theta^0_{\mathrm{O}^{2-}}} + \frac{Ne\mu}{\varepsilon_0}\left\{\left(\theta_{\mathrm{O}^{2-}} - \theta^0_{\mathrm{O}^{2-}}\right) + \frac{\pi\sqrt{3}}{16}\frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}}\left(\theta^{3/2}_{\mathrm{O}^{2-}} - \theta^{0\,3/2}_{\mathrm{O}^{2-}}\right)\right\}. \qquad [20]$$

If we compare Eq. [16] to Eq. [2] we see that, in general, the outer potential will depend upon the chemical potential and lateral interaction terms,

$$e\Delta\Psi = \frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}} + e\Delta V_{\mathrm{lat,O}^{2-}}, \qquad [21]$$

or

$$e\Delta\Psi = \frac{kT}{2}\ln\frac{\theta_{\mathrm{O}^{2-}}}{\theta_*}\frac{\theta^0_*}{\theta^0_{\mathrm{O}^{2-}}} + \frac{Ne\mu}{\varepsilon_0} \times \frac{\pi\sqrt{3}}{16}\frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}}\left(\theta^{3/2}_{\mathrm{O}^{2-}} - \theta^{0\,3/2}_{\mathrm{O}^{2-}}\right). \qquad [22]$$

As oxygen is electrophilic, oxygen-ion coverages cannot be very low under open-circuit conditions and, because of the Weisz limitation (21), oxygen-ion coverages cannot be very high under open-circuit conditions. Provided that the ionic oxygen coverage is also not very high or very low under closed-circuit conditions, we may neglect changes in the logarithimic terms of coverage as

$$\frac{N\mu}{\varepsilon_0} \gg \frac{kT}{e},$$

and the surface potential and lateral interaction terms have a stronger dependency on coverage. (Typical values of dipole moments for surface ions indicate that $N\mu/\varepsilon_0$ will be of the order of tens of volts whereas kT/e will be of the order of tens of millivolts.) Therefore, for intermediate oxygen-ion coverages (obtained at intermediate overpotentials),

$$\Delta\mu_{\mathrm{O}^{2-}} \approx 0, \qquad [23]$$

and

$$e\eta \approx \frac{Ne\mu}{\varepsilon_0}\left\{\left(\theta_{\mathrm{O}^{2-}} - \theta^0_{\mathrm{O}^{2-}}\right) + \frac{\pi\sqrt{3}}{16}\frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}}\left(\theta^{3/2}_{\mathrm{O}^{2-}} - \theta^{0\,3/2}_{\mathrm{O}^{2-}}\right)\right\},$$

and the change in outer potential can be seen to be,

$$e\Delta\Psi \approx \frac{Ne\mu}{\varepsilon_0}\frac{\pi\sqrt{3}}{16}\frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}}\left(\theta^{3/2}_{\mathrm{O}^{2-}} - \theta^{0\,3/2}_{\mathrm{O}^{2-}}\right).$$

It can easily be shown that

$$\frac{d\Delta\Psi}{d\eta} \approx \frac{\frac{3\pi\sqrt{3}}{32}\frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}}\theta^{1/2}_{\mathrm{O}^{2-}}}{1 + \frac{3\pi\sqrt{3}}{32}\frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}}\theta^{1/2}_{\mathrm{O}^{2-}}}.$$

For a spherical oxygen ion ($a_{\mathrm{O}^{2-}} = 2r_{\mathrm{O}^{2-}}$) at a coverage of 0.01, this gradient, $d\Delta\Psi/\mathrm{d}\eta$, has a value of $\sim$0.1 indicating that even at this low ionic oxygen coverage the change in outer potential will be equal to about 10% of any applied overpotential.

Equation [20] shows that in the case of closed-circuit operation the Weisz limitation (21) need no longer hold and Eq. [23] is not always valid. In theory the electrochemical driving force can be used to dramatically increase (or decrease) the coverage of the ionic species. In the case of oxygen supply $\Delta\chi$ will reach a maximum value (when oxygen ions have reached full coverage) after which changes in overpotential will only result in further changes in outer potential. For large positive overpotentials,

$$e\Delta\chi^{\max} = \frac{\Delta\sigma^{\max}\mu}{2\varepsilon_0} = \frac{(\sigma^{\max} - \sigma^0)\mu}{2\varepsilon_0},$$

with

$$\sigma^{\max} = 2Ne$$
$$\sigma^0 = 2Ne\theta^0_{\mathrm{O}^{2-}}.$$

Therefore, for $\eta > \eta^{\max}$, where $\eta^{\max}$ refers to the value of the overpotential as the surface potential approaches its maximum value,

$$e\Delta\Psi = e\eta - e\Delta\chi^{\max}.$$

In the case of oxygen removal $\Delta\chi$ will reach a threshold value (when all of the oxygen ions have been removed) after which changes in overpotential will only result in changes in outer potential driving the ion coverage to very low values. For large negative overpotentials,

$$e\Delta\chi^{\min} = \frac{\Delta\sigma^{\min}\mu}{2\varepsilon_0} = \frac{-\sigma^0\mu}{2\varepsilon_0},$$

and for $\eta < \eta^{\min}$, where $\eta^{\min}$ refers to the value of the overpotential as the surface potential approaches its minimum value,

$$e\Delta\Psi = e\eta - e\Delta\chi^{\min}.$$

(We will define intermediate overpotentials to be overpotentials between $\eta^{\min}$ and $\eta^{\max}$ (intermediate oxygen-ion coverages are the corresponding values of coverage). Outside of this region we refer to large (or very) positive overpotentials and large (or very) negative overpotentials with corresponding very high and very low oxygen-ion coverages.)

We may comment on the difference in $\eta^{\max}$ and $\eta^{\min}$ as

$$e\Delta\chi^{\max} - e\Delta\chi^{\min} = \frac{\sigma^{\max}\mu}{2\varepsilon_0} = \frac{Ne\mu}{\varepsilon_0},$$

and therefore the difference between the maximum and minimum values of surface potential will be of the order of tens of volts (21). Likewise the difference between the values of $\eta^{\max}$ and $\eta^{\min}$ will be of the order of tens of volts. As a result of the Weisz limitation $\eta^{\min}$ will be negative and of the order of a volt or so depending upon the energetics of oxygen-ion formation; hence $\eta^{\max}$ will be positive and must be of the order of tens of volts.

We now know how overpotential, surface potential and outer potential are related at steady state. For intermediate ion coverages logarithmic terms in coverage can be neglected,

$$\Delta\mu_{\mathrm{O}^{2-}} \approx 0.$$

If the ionic coverage is low enough that lateral interactions are negliglible then there is a change in surface potential equal to the applied overpotential, use of Eq. [16] gives

$$e\Delta\chi \approx e\eta. \qquad [24]$$

At higher intermediate ion coverages the change in surface potential no longer matches the applied overpotential due to appreciable lateral interactions. At very low ion coverages the surface potential reaches a minimum value and thereafter can be modified no further. Likewise, at very high ion coverages the surface potential reaches a maximum coverage and can be modified no further. Figures 2 and 3 are sketches of how surface potential and outer potential depend on applied overpotential.

One of the key observations from past work (e.g., 1) is that the change in extraction potential is often equal

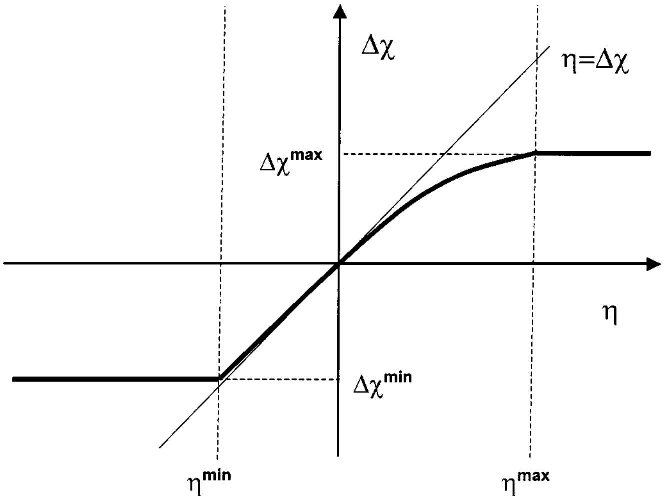

FIG. 2. Change in surface potential versus applied overpotential.

to the applied overpotential in solid–electrolyte supported systems (although there are important exceptions to this behaviour (17–20)). The above model suggests that in the case of Reaction 2 being at equilibrium, a surface would in general be expected to show this direct relationship between overpotential and change in extraction potential at appropriate overpotentials. However, this relationship fails at high intermediate ionic coverages when lateral electrostatic interactions become important or at very low ionic coverages when ionic coverages can no longer be decreased due to a lack of availability of surface oxygen ions.

3. REACTION RATE MODIFICATION

Let us consider a reaction between adsorbed surface species,

$$A + B \rightarrow C, \qquad \text{[Reaction 7]}$$

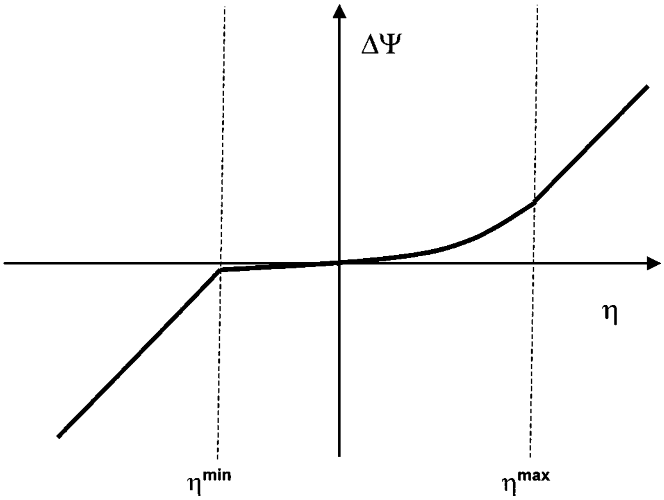

FIG. 3. Change in outer potential versus applied overpotential.

where either A or B could be atomic surface oxygen but do not need to be. Vayenas (e.g., 1), has suggested that the surface reaction rate may depend upon a rate-determining step involving electron transfer between the catalyst and an adsorbed reactant, in this case either A or B. Here we use this idea of the importance of electron transfer to or from the reactants to develop a simple reaction rate model based on transition state theory. Oxygen ion supply or removal from the surface is considered to modify equilibria involving electron supply or removal by altering the surface potential of the catalyst and modifying the potential of electrons associated with the surface O/O^{2-} redox couple, hence only long-range electrostatic interactions are invoked to describe rate modification.

Reaction 7 can proceed in the absence of charge transfer with the catalyst or other adsorbates, through the following fundamental steps. The reactants are in equilibrium with a reactive transition state, AB,

$$A + B \Leftrightarrow AB, \qquad \text{[Reaction 8]}$$

with the rate of decomposition of the transition state into the product being the rate-determining step,

$$AB \rightarrow C. \qquad \text{[Reaction 9]}$$

The rate of Reaction 9 is assumed to depend linearly on the coverage of AB,

$$r_9 = k_9\theta_{AB}, \qquad [25]$$

with the coverage determined by the equilibrium of Reaction 8,

$$\theta_{AB} = K_8\theta_A\theta_B, \qquad [26]$$

and the rate of Reaction 9 can be written as

$$r_9 = k_9K_8\theta_A\theta_B. \qquad [27]$$

Now let us consider a reaction proceeding through a negatively charged transition state. We explain the modified reaction rate in terms of a modification in the coverage of the charged transition state formed by the reaction of A^- with B, A^-B, or of A with B^-, AB^- (we restate our assumption that the coverage of such charged transition states is much lower than that of oxygen ions and therefore their effect on the properties of the surface double layer may be neglected). There are two sources of electrons for the modification of reaction rate, the catalyst and adsorbed oxygen ions themselves. (Vayenas and co-workers have defined an electrophilic reaction as one promoted by a greater availability of electrons from the metal catalyst as determined by the surface potential. Note that a negatively-charged transition state is formally different from an electrophilic reaction because of the possibility of electron donation from the adsorbed O/O^{2-} redox couple as well as the metal). For the purposes of illustration let us suppose that the species

A equilibrates with electrons from the catalyst to form A^- while the species B equilibrates with surface oxygen ions to form the species B^-. Hence we have two reaction schemes,

$$A + e^- \Leftrightarrow A^- \qquad \text{[Reaction 10]}$$

$$A^- + B \Leftrightarrow A^-B \qquad \text{[Reaction 11]}$$

$$A^-B \rightarrow C + e^-, \qquad \text{[Reaction 12]}$$

and

$$B + \frac{1}{2}O^{2-} \Leftrightarrow B^- + \frac{1}{2}O \qquad \text{[Reaction 13]}$$

$$A + B^- \Leftrightarrow AB^- \qquad \text{[Reaction 14]}$$

$$AB^- \rightarrow C + e^-_{\mathrm{surf}} \qquad \text{[Reaction 15]}$$

$$e^-_{\mathrm{surf}} + \frac{1}{2}O \rightarrow \frac{1}{2}O^{2-}, \qquad \text{[Reaction 16]}$$

where e^-_{surf} is an electron associated with the metal surface rather than the metal bulk. (Here we consider A^-B and AB^- to have distinct chemical identities; however, we could equally well consider them to be chemically identical but analysis would be much more complex in this case as the transition state cannot be in equilibrium with all of the reactants under closed-circuit operation.) It should be noted that if the second scheme finished with the reaction

$$AB^- \rightarrow C + e^-, \qquad \text{[Reaction 17]}$$

then the scheme could not cause a non-Faradaic change in reaction rate as one surface oxygen ion would be consumed by each catalytic cycle. (Many other reaction schemes could be suggested but here we use a simple scheme that is able to account for behaviour in the case of a negatively charged transition state and the possibility of electron donation from both the metal and the adsorbed O/O^{2-} redox couple.)

In addition, under open-circuit conditions, the following equilibrium will hold:

$$AB^- \Leftrightarrow A^-B. \qquad \text{[Reaction 18]}$$

Note that this equilibrium will not hold under closed-circuit conditions because of the difference in electrochemical potential between catalyst electrons and electrons associated with the O/O^{2-} redox couple.

We can write the overall reaction rate, r_-(to denote a negatively charged transition state is important) as

$$r_- = r_9 + r_{12} + r_{15}, \qquad [28]$$

and if all reaction rates have a linear dependence on the coverage of the transition state,

$$r_- = k_9\theta_{AB} + k_{12}\theta_{A^-B} + k_{15}\theta_{AB^-}. \qquad [29]$$

As under open-circuit conditions,

$$r_-^0 = r_9^0 + r_{12}^0 + r_{15}^0. \qquad [30]$$

Equation [28] can be re-expressed in the form

$$r_- = r_9^0 + r_{12}^0\frac{\theta_{A^-B}}{\theta^0_{A^-B}} + r_{15}^0\frac{\theta_{AB^-}}{\theta^0_{AB^-}}. \qquad [31]$$

We now consider how the ratios $\theta_{A^-B}/\theta^0_{A^-B}$ and $\theta_{AB^-}/\theta^0_{AB^-}$ depend upon overpotential. The condition of equilibrium for Reaction 10 gives

$$\bar{\mu}_{A^-} = \mu_A + \bar{\mu}_e \qquad [32]$$

$$\bar{\mu}_{A^-} = \mu_A + \mu_e - e\phi \qquad [33]$$

where chemical and electrochemical potentials for A and B refer to the surface species. Equilibrium for Reaction 11 gives

$$\bar{\mu}_{A^-B} = \bar{\mu}_{A^-} + \mu_B. \qquad [34]$$

Combining Eqs. [33] and [34],

$$\bar{\mu}_{A^-B} = \mu_A + \mu_e - e\phi + \mu_B, \qquad [35]$$

or

$$\mu_{A^-B} - e\phi_{A^-B} = \mu_A + \mu_e - e\phi + \mu_B, \qquad [36]$$

where ϕ_{A^-B} is the potential of electrons associated with the A^-B species.

After Eq. [17], the change in the chemical potential of A^-B is given by

$$\Delta\mu_{A^-B} = kT\ln\frac{\theta_{A^-B}}{\theta_*}\frac{\theta_*^0}{\theta^0_{A^-B}}.$$

Provided that the chemical potentials of surface A and B are not modified, i.e., gas-phase chemical potentials are constant (differential reactor operation) and there are fast adsorption and desorption processes, Eq. [36] gives

$$\Delta\mu_{A^-B} = e\Delta\phi_{A^-B} - e\Delta\phi,$$

and therefore,

$$kT\ln\frac{\theta_{A^-B}}{\theta^0_{A^-B}}\frac{\theta_*^0}{\theta_*} = e\Delta\phi_{A^-B} - e\Delta\phi.$$

However, the change in potential difference between electrons associated with the A^-B species and the metal depends upon changes in the surface potential and changes in the potential associated with lateral interactions. Remembering that to form the A^-B species an electron need not cross the entire double layer (provided that the charge separation for the A^-B species is less than that for the ionic oxygen), then, as the average field is constant between the sheets of charge associated with the metal and the oxygen ions,

$$\phi_{\mathrm{A^-B}} = \phi - \frac{a_{\mathrm{A^-B}}}{a_{\mathrm{O^{2-}}}}\chi - V_{\mathrm{lat,A^-B}},$$

where $a_{\mathrm{A^-B}}$ is the charge separation associated with the $\mathrm{A^-B}$ species, and

$$e\Delta\phi_{\mathrm{A^-B}} - e\Delta\phi = -\frac{a_{\mathrm{A^-B}}}{a}e\Delta\chi - e\Delta V_{\mathrm{lat,A^-B}}.$$

The lateral dipole–dipole interaction potential was previously found to be (21)

$$V_{\mathrm{lat,A^-B}} = \frac{N\mu}{\varepsilon_0}\frac{\pi\sqrt{3}}{16}\frac{a_{\mathrm{A^-B}}}{r_{\mathrm{O^{2-}}}}\theta_{\mathrm{O^{2-}}}^{3/2}. \qquad [37]$$

As a result of the potential due to lateral interactions depending linearly on dipole separation, we may write

$$V_{\mathrm{lat,A^-B}} = \frac{a_{\mathrm{A^-B}}}{a_{\mathrm{O^{2-}}}}V_{\mathrm{lat,O^{2-}}}. \qquad [38]$$

Therefore,

$$\Delta V_{\mathrm{lat,A^-B}} = \frac{a_{\mathrm{A^-B}}}{a_{\mathrm{O^{2-}}}}\Delta V_{\mathrm{lat,O^{2-}}},$$

so

$$e\Delta\phi_{\mathrm{A^-B}} - e\Delta\phi = -\frac{a_{\mathrm{A^-B}}}{a_{\mathrm{O^{2-}}}}\left(e\Delta\chi + e\Delta V_{\mathrm{lat,O^{2-}}}\right),$$

or, using Eq. [16],

$$e\Delta\phi_{\mathrm{A^-B}} - e\Delta\phi = -\frac{a_{\mathrm{A^-B}}}{a_{\mathrm{O^{2-}}}}\left(e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}}\right).$$

Therefore,

$$kT\ln\frac{\theta_{\mathrm{A^-B}}}{\theta^0_{\mathrm{A^-B}}}\frac{\theta^0_*}{\theta_*} = -\frac{a_{\mathrm{A^-B}}}{a_{\mathrm{O^{2-}}}}\left(e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}}\right),$$

and

$$\begin{aligned} r_{12} &= r^0_{12}\frac{\theta_{\mathrm{A^-B}}}{\theta^0_{\mathrm{A^-B}}} \\ r_{12} &= r^0_{12}\frac{\theta_*}{\theta^0_*}\exp\frac{1}{kT}\left\{-\frac{a_{\mathrm{A^-B}}}{a_{\mathrm{O^{2-}}}}\left(e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}}\right)\right\}. \end{aligned} \qquad [39]$$

Now we consider the modification of the rate of Reaction 15 in a similar manner. Equilibrium for Reaction 13 gives

$$2\mu_{\mathrm{B}} + \bar{\mu}_{\mathrm{O^{2-}}} = 2\bar{\mu}_{\mathrm{B^-}} + \mu_{\mathrm{O}} \qquad [40]$$

$$\bar{\mu}_{\mathrm{AB^-}} = \mu_{\mathrm{A}} + \bar{\mu}_{\mathrm{B^-}}. \qquad [41]$$

Combining Eqs. [40] and [41],

$$\bar{\mu}_{\mathrm{AB^-}} = \mu_{\mathrm{A}} + \mu_{\mathrm{B}} + \frac{1}{2}\bar{\mu}_{\mathrm{O^{2-}}} - \frac{1}{2}\mu_{\mathrm{O}}, \qquad [42]$$

or

$$\mu_{\mathrm{AB^-}} - e\phi_{\mathrm{AB^-}} = \mu_{\mathrm{A}} + \mu_{\mathrm{B}} + \frac{1}{2}\mu_{\mathrm{O^{2-}}} - e\phi_{\mathrm{O^{2-}}} - \frac{1}{2}\mu_{\mathrm{O}}, \qquad [43]$$

where $\phi_{\mathrm{AB^-}}$ is the potential of electrons associated with the $\mathrm{AB^-}$ species.

After Eq. [17], the change in the chemical potential of $\mathrm{AB^-}$ is given by

$$\Delta\mu_{\mathrm{AB^-}} = kT\ln\frac{\theta_{\mathrm{AB^-}}}{\theta_*}\frac{\theta^0_*}{\theta^0_{\mathrm{AB^-}}}.$$

Provided that the chemical potentials of surface A and B are not modified, Eq. [43] gives

$$\Delta\mu_{\mathrm{AB^-}} = e\Delta\phi_{\mathrm{AB^-}} - e\Delta\phi_{\mathrm{O^{2-}}} + \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}} - \frac{1}{2}\Delta\mu_{\mathrm{O}},$$

and therefore,

$$kT\ln\frac{\theta_{\mathrm{AB^-}}}{\theta^0_{\mathrm{AB^-}}}\frac{\theta^0_*}{\theta_*} = e\Delta\phi_{\mathrm{AB^-}} - e\Delta\phi_{\mathrm{O^{2-}}} + \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}} - \frac{1}{2}\Delta\mu_{\mathrm{O}}.$$

Again, as electrons from the oxygen ions do not cross the entire double layer on formation of $\mathrm{AB^-}$,

$$\begin{aligned} e\Delta\phi_{\mathrm{AB^-}} - e\Delta\phi_{\mathrm{O^{2-}}} = {} & \frac{a_{\mathrm{O^{2-}}} - a_{\mathrm{AB^-}}}{a_{\mathrm{O^{2-}}}}e\Delta\chi + \Delta V_{\mathrm{lat,O^{2-}}} \\ & - e\Delta V_{\mathrm{lat,AB^-}}. \end{aligned}$$

But after Eq. [38],

$$\Delta V_{\mathrm{lat,AB^-}} = \frac{a_{\mathrm{AB^-}}}{a_{\mathrm{O^{2-}}}}\Delta V_{\mathrm{lat,O^{2-}}}, \qquad [44]$$

so

$$e\Delta\phi_{\mathrm{AB^-}} - e\Delta\phi_{\mathrm{O^{2-}}} = \frac{a_{\mathrm{O^{2-}}} - a_{\mathrm{AB^-}}}{a_{\mathrm{O^{2-}}}}\left(e\Delta\chi + e\Delta V_{\mathrm{lat,O^{2-}}}\right),$$

or

$$e\Delta\phi_{\mathrm{AB^-}} - e\Delta\phi_{\mathrm{O^{2-}}} = \frac{a_{\mathrm{O^{2-}}} - a_{\mathrm{AB^-}}}{a_{\mathrm{O^{2-}}}}\left(e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}}\right).$$

Therefore,

$$\begin{aligned} kT\ln\frac{\theta_{\mathrm{AB^-}}}{\theta^0_{\mathrm{AB^-}}}\frac{\theta^0_*}{\theta_*} = {} & \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}} - \frac{1}{2}\Delta\mu_{\mathrm{O}} \\ & + \frac{a_{\mathrm{O^{2-}}} - a_{\mathrm{AB^-}}}{a_{\mathrm{O^{2-}}}}\left(e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}}\right), \end{aligned}$$

and

$$r_{15} = r_{15}^{0}\frac{\theta_{AB^-}}{\theta_{AB^-}^{0}}$$

$$r_{15} = r_{15}^{0}\frac{\theta_*}{\theta_*^{0}}\exp\frac{1}{kT}\left\{\frac{1}{2}\Delta\mu_{O^{2-}} - \frac{1}{2}\Delta\mu_{O} + \frac{a_{O^{2-}} - a_{AB^-}}{a_{O^{2-}}}\left(e\eta - \frac{1}{2}\Delta\mu_{O^{2-}}\right)\right\}. \quad [45]$$

Now let us consider a reaction proceeding through a positively charged transition state. Again we explain the change in reaction rate in terms of a modification in the coverage of the charged transition state formed by the reaction of A^+ with B, A^+B, or of A with B^+, AB^+. There are two sinks for electrons for the modification of reaction rate, the catalyst and neutral adsorbed oxygen. For the purposes of illustration let us suppose that the species A equilibrates with electrons from the catalyst to form A^+ while the species B equilibrates with surface oxygen to form the species B^+. Hence we have two reaction schemes,

$$A \Leftrightarrow A^+ + e^- \quad \text{[Reaction 19]}$$

$$A^+ + B \Leftrightarrow A^+B \quad \text{[Reaction 20]}$$

$$A^+B \rightarrow C + h^+ \quad \text{[Reaction 21]}$$

$$h^+ + e^- \rightarrow 0, \quad \text{[Reaction 22]}$$

where h^+ signifies an electron hole, and

$$B + \frac{1}{2}O \Leftrightarrow B^+ + \frac{1}{2}O^{2-} \quad \text{[Reaction 23]}$$

$$A + B^+ \Leftrightarrow AB^+ \quad \text{[Reaction 24]}$$

$$AB^+ \rightarrow C + h^+ \quad \text{[Reaction 25]}$$

$$h^+ + \frac{1}{2}O^{2-} \rightarrow \frac{1}{2}O. \quad \text{[Reaction 26]}$$

Here we once again consider A^+B and AB^+ to have distinct chemical identities.

We can write the overall reaction rate, r_+ (to denote a positively charged transition state is important) as

$$r_+ = r_9 + r_{21} + r_{25} \quad [46]$$

$$r_+ = k_9\theta_{AB} + k_{21}\theta_{A^+B} + k_{25}\theta_{AB^+}. \quad [47]$$

As under open-circuit conditions,

$$r_+^{0} = r_9^{0} + r_{21}^{0} + r_{25}^{0}. \quad [48]$$

Equation [46] can be re-expressed in the form

$$r_+ = r_9^{0} + r_{21}^{0}\frac{\theta_{A^+B}}{\theta_{A^+B}^{0}} + r_{25}^{0}\frac{\theta_{AB^+}}{\theta_{AB^+}^{0}}. \quad [49]$$

A similar analysis as before leads to

$$r_{21} = r_{21}^{0}\frac{\theta_*}{\theta_*^{0}}\exp\frac{1}{kT}\left\{\frac{a_{A^+B}}{a_{O^{2-}}}\left(e\eta - \frac{1}{2}\Delta\mu_{O^{2-}}\right)\right\} \quad [50]$$

$$r_{25} = r_{25}^{0}\frac{\theta_*}{\theta_*^{0}}\exp\frac{1}{kT}\left\{\frac{1}{2}\Delta\mu_{O} - \frac{1}{2}\Delta\mu_{O^{2-}} - \frac{a_{O^{2-}} - a_{AB^+}}{a_{O^{2-}}} \times\left(e\eta - \frac{1}{2}\Delta\mu_{O^{2-}}\right)\right\}. \quad [51]$$

Now let us consider how the overall reaction rate will depend on overpotential (detailed mathematical analyses is presented in Appendices A and B for the cases of negatively and positively charged transition states respectively). We assume that the chemical potential of adsorbed oxygen is constant. (However, in addition to Reaction 2 being at equilibrium it is instructive to consider what happens if Reaction 1 is also at equilibrium (therefore Reaction 3 must be at equilibrium). This case is discussed in Appendix C.)

Any reactions which do not depend upon charge transfer with the metal or the oxygen redox couple, i.e., take place between neutral adsorbed species, will be unaffected by electrode polarisation,

$$r_9 = r_9^{0}. \quad [52]$$

For a negatively charged transition state,

$$r_- = r_9 + r_{12} + r_{15},$$

and at negative overpotentials Reaction 12 may dominate as a result of the reduced surface potential and the increased ease of donation of electrons from the metal. At large negative overpotentials it is no longer possible to modify the surface potential or the lateral interaction potential as the coverage of oxygen ions approaches zero. Likewise it is no longer possible to modify the rate of Reaction 12. At positive overpotentials Reaction 15 may dominate as a result of electron donation from oxygen ions through Reaction 13. At large positive overpotentials the rate of Reaction 15 will go through a maximum as the coverage of ionic oxygen approaches unity. Figure 4 shows the approximate form of the rate versus overpotential behaviour with the reactions requiring electron transfer being much slower than the reaction which does not require electron transfer under open-circuit conditions. Reaction rate increases at both positive and negative overpotentials as a result of electron donation from the O/O^{2-} redox couple and the metal.

For reactions involving positively charged transition states at negative overpotentials Reaction 25 may dominate as a result of electron donation to adsorbed oxygen through Reaction 23. At positive overpotentials Reaction 21 may dominate as a result of electron donation to the metal through Reaction 19. Figure 5 shows the approximate form of the expected rate versus overpotential behaviour.

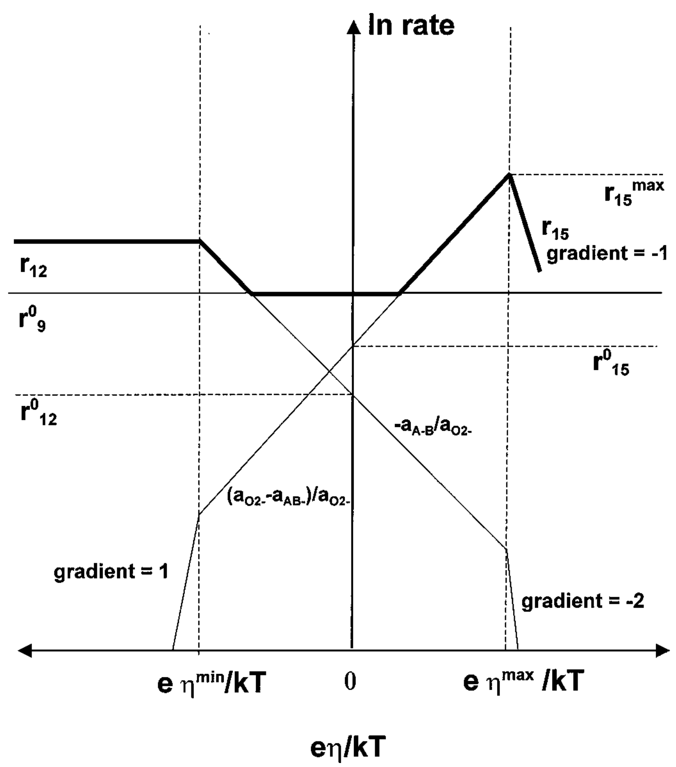

FIG. 4. Schematic of reaction rate versus overpotential in the case of a negatively charged transition state.

Again the reaction rate will eventually increase for both large positive and negative overpotentials with the rate of Reaction 21 going through a maximum as the coverage of ionic oxygen approaches unity.

Importantly, this overpotential-reaction rate behaviour for both negatively and positively charged transition states is similar to that observed in some experimental studies (e.g., 1, 2) where reaction rate is seen to increase both at positive overpotentials and negative overpotentials.

The above determined dependencies of the reaction rates for the formation of AB on overpotential (in the case of $\Delta\mu_{\mathrm{O}}$ approximately equal to zero, fast Reactions 4 and 5) can be expressed in simple approximate forms under conditions where one reaction dominates. Again, in the case of reactions requiring electron transfer being slower than those which do not need electron transfer under open-circuit conditions,

$$\frac{r}{r^0} \approx \exp\left(\frac{\alpha e\eta}{kT}\right)\exp\left(-\frac{\alpha e\eta^*}{kT}\right), \qquad [53]$$

where α is related to the effective gradient of the relationships shown in Figs. 4 and 5 and the constant $\exp(-\alpha e\eta^*/kT)$ includes any overpotential, η^*, that needs to be overcome before the overall reaction rate is modified. As the catalyst surface is macroscopically uniform as a result of fast surface diffusion of species, total rates are proportional to area specific reaction rates. In addition for intermediate overpotentials in the absence of lateral interactions, the applied overpotential is equal to the change in extraction potential. Hence manipulation of Eq. [53] yields Eq. [3].

In the case of simplification of Eq. [50], for the rate of Reaction 21 in the region of intermediate overpotentials, Eq. [B2] is obtained (see Appendix B),

$$r_{21} \approx r_{21}^0 \exp\left(\frac{a_{\mathrm{A^+B}}}{a_{\mathrm{O^{2-}}}}\frac{e\eta}{kT}\right). \qquad [54]$$

For a positively charged transition state the total rate of production of AB depends upon the sum of the individual rates,

$$\frac{r}{r^0} = \frac{r_{21}+r_{25}+r_9}{r^0}. \qquad [55]$$

For reasonably large positive overpotentials such that the rate of Reactions 25 and 9 can be neglected,

$$\frac{r}{r^0} \approx \frac{r_{21}^0}{r^0}\exp\left(\frac{a_{\mathrm{A^+B}}}{a_{\mathrm{O^{2-}}}}\frac{e\eta}{kT}\right), \qquad [56]$$

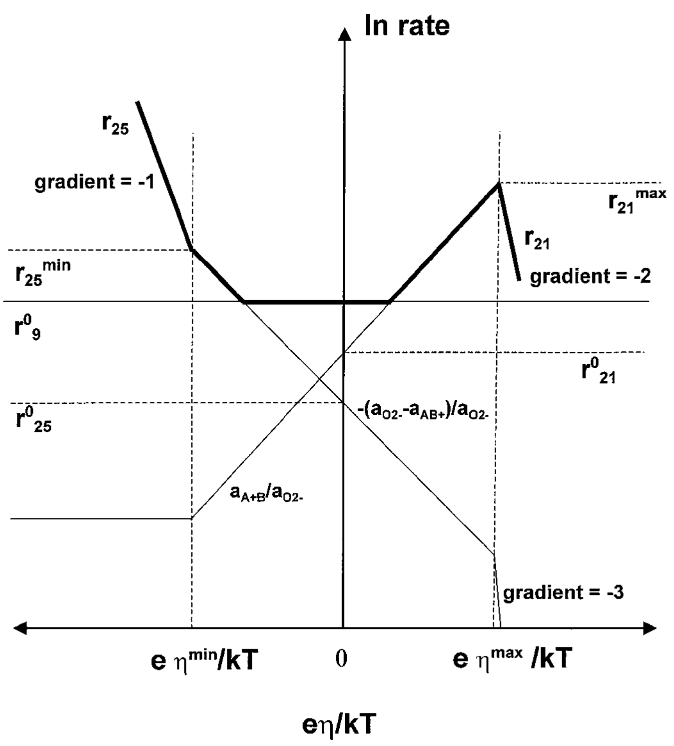

FIG. 5. Schematic of reaction rate versus overpotential in the case of a positively charged transition state.

and therefore comparing with Eq. [53],

$$\exp\left(-\frac{\alpha e\eta^*}{kT}\right) = \frac{r_{21}^0}{r^0} \quad [57]$$

$$\alpha = \frac{a_{\mathrm{A^+B}}}{a_{\mathrm{O^{2-}}}}. \quad [58]$$

If the rate modification is large enough, then

$$\frac{\Delta r}{r^0} \approx \frac{r}{r^0} \approx \frac{r_{21}^0}{r^0}\exp\left(\frac{a_{\mathrm{A^+B}}}{a_{\mathrm{O^{2-}}}}\frac{e\eta}{kT}\right). \quad [59]$$

In the case of α equal to unity (i.e., the same charge separation for the transition state and the oxygen ion) and again with total rates being proportional to area specific reaction rates, Eq. [59] becomes

$$\Delta R \approx R^0 \exp\left(\frac{e\eta}{kT}\right)\frac{R_{21}^0}{R^0}, \quad [60]$$

and returning to Eq. [4],

$$\Lambda = \frac{2F\Delta R}{I} \approx \frac{2FR^0}{I}\exp\left(\frac{e\eta}{kT}\right)\frac{R_{21}^0}{R^0}. \quad [61]$$

Let us consider the reaction network presented in Part I (21). The measured current will be predominantly due to Reaction 1 (if the exchange current for this reaction is much higher than that for either Reactions 2 or 3),

$$I \approx I_1, \quad [62]$$

and using the high-field form of the Butler–Volmer equation with a symmetry factor of one-half,

$$I_1 = I_{0,1}\exp\left(\frac{e\eta}{kT}\right). \quad [63]$$

Furthermore,

$$I_0 \approx I_{0,1}. \quad [64]$$

Combining Eqs. [62], [63], and [64],

$$I \approx I_0 \exp\left(\frac{e\eta}{kT}\right). \quad [65]$$

Substituting Eq. [65] into [61],

$$\Lambda \approx \frac{2FR^0}{I_0}\frac{R_{21}^0}{R^0}, \quad [66]$$

which is similar to the relationship that Vayenas (1) has indicated can be used to estimate the enhancement factor,

$$|\Lambda| \approx \frac{2FR^0}{I_0}, \quad [67]$$

with the factor R_{21}^0/R^0 included to allow for the fact that reaction through the charged transition state is not necessarily responsible for the entire open-circuit reaction rate.

We may proceed further with the analysis to gain some insight into the physical origin of the enhancement factor. In the case of a catalyst that shows an extraction potential change equal to the applied overpotential we have already argued that the spillover oxygen must be stable and hence the kinetics for Reaction 6 slow (21). If we assume on polarisation (and at steady state) that ionic oxygen is supplied to solely overcome decomposition through Reaction 3 then a material balance performed on the spillover species gives

$$I_2 \approx I_3, \quad [68]$$

and Reaction 3 can be represented by a charge-transfer reaction with the driving force depending upon the difference in the redox potential of the O/O^{2-} couple and the electron potential, η_3. As Reactions 2, 4, and 5 are fast the overpotential for Reaction 3 is approximately equal to the applied overpotential. Using a high-field approximation, again with a symmetry factor of one-half,

$$I_2 \approx I_3 = I_{0,3}\exp\left(\frac{e\eta_3}{kT}\right) \approx I_{0,3}\exp\left(\frac{e\eta}{kT}\right). \quad [69]$$

We may define a selectivity for formation of ionic oxygen by charge transfer as

$$S_{\mathrm{ct}} = \frac{I_2}{I}. \quad [70]$$

Using Eqs. [65] and [69], this becomes

$$S_{\mathrm{ct}} \approx \frac{I_{0,3}\exp\left(\frac{e\eta}{kT}\right)}{I_0\exp\left(\frac{e\eta}{kT}\right)} \approx \frac{I_{0,3}}{I_0}. \quad [71]$$

Let us assume that oxygen desorption can be neglected and let the selectivity for ionic oxygen formation from adsorbed oxygen (the competing reaction being adsorbed oxygen removal by Reaction 5) be S_{surf}. S_{surf} therefore depends upon the rate of the reverse of Reaction 3 and we may define a selectivity for formation of ionic oxygen from adsorbed oxygen, based upon open-circuit operating conditions, as

$$S_{\mathrm{surf}} = \frac{I_{0,3}}{2FR_5^0}. \quad [72]$$

Combining these definitions and substituting into Eq. (66) gives

$$\Lambda \approx \frac{S_{\mathrm{ct}}}{S_{\mathrm{surf}}}\frac{R^0}{R_5^0}\frac{R_{21}^0}{R^0}. \quad [73]$$

In the case of oxygen being one of the reactants, A or B, then, as the reaction of oxygen ions (Reaction 6) does not contribute significantly to the overall rate, the loss of neutral adsorbed oxygen from the surface is the same process as the production of AB,

$$R_5 = R, \tag{74}$$

and

$$R_5^0 = R^0. \tag{75}$$

Hence,

$$\Lambda \approx \frac{S_{\mathrm{ct}}}{S_{\mathrm{surf}}} \frac{R_{21}^0}{R^0}. \tag{76}$$

As one might intuitively expect, high selectivities for ionic oxygen formation as a result of the charge-transfer process will lead to high enhancement factors. High selectivities for ionic oxygen formation from adsorbed oxygen will cause low enhancement factors. It is also important that reactions proceeding through charged transition states contribute significantly to the open-circuit rate for enhancement factors to be large.

4. CONCLUSIONS

A simple model to describe the reversible electrochemical promotion of supported catalysts has been formulated. This model is derived from first principles and allows for the presence of two forms of surface oxygen, one ionic and one neutral. Both forms of surface oxygen are able to undergo charge-transfer reactions with the solid–electrolyte support. The ionic oxygen is assumed to be the only ion present with a significant surface coverage and, as such, dictates the properties of the catalyst surface double layer. By describing changes in surface potential with the Helmholtz equation and considering lateral dipole–dipole interactions a relationship between the electrode overpotential and the coverage of oxygen ions was found for the case of a stable ionic oxygen spillover species. This equation was then used to predict how surface potential and outer potential would vary on application of an overpotential to the catalyst/support interface. In the presence of significant lateral interactions the change in surface potential must be less than the applied overpotential. Furthermore, by considering a simple reaction mechanism that involves a charged transition state and accounting for the effect of long-range electrostatic interactions it was possible to express reaction rates as a function of applied overpotential. Electron donation and acceptance from the metal catalyst and the surface O/O^{2-} redox couple were both considered. It is shown that under certain conditions reaction rates are predicted to increase on application of both negative and positive overpotentials (for both positively charged and negatively charged transition states) in agreement with some experimental studies (e.g., 1, 2). In addition the enhancement factor is shown to depend upon the selectivity for oxygen ion formation from charge-transfer and adsorption processes.

APPENDIX I: REACTION RATE AS A FUNCTION OF OVERPOTENTIAL FOR A NEGATIVELY CHARGED TRANSITION STATE

Provided that overpotentials are negative or intermediate (less than or equal to $\eta^{\max}$) then the coverage of vacant sites will not change greatly and we may use the approximation

$$\theta_* \approx \theta_*^0. \tag{A1}$$

However, at large positive overpotentials oxygen ions are forced onto the surface at very high coverage, approaching unity, and the coverage of vacant sites is greatly reduced. Using Eq. [17] with the coverage of oxygen ions approximately equal to unity and therefore constant gives

$$\Delta\mu_{O^{2-}} \approx kT \ln \frac{\theta_*^0}{\theta_*},$$

and, therefore,

$$\frac{\theta_*}{\theta_*^0} \approx \exp\left(-\frac{\Delta\mu_{O^{2-}}}{kT}\right). \tag{A2}$$

Consequently, the reaction rate expressions (Eqs. [39], [45], [50], and [51]) must be combined with Eqs. [A1] or [A2] depending upon the regime of operation.

Let us consider how the reaction rates will depend on overpotential. We assume that the chemical potential of adsorbed oxygen is constant. Provided that $\eta^{\min} \leq \eta \leq \eta^{\max}$, i.e., intermediate overpotentials, then, restating Eq. [23],

$$\Delta\mu_{O^{2-}} \approx 0,$$

and

$$e\eta - \frac{1}{2}\Delta\mu_{O^{2-}} \approx e\eta,$$

with Eq. [A1] being obeyed,

$$\theta_* \approx \theta_*^0.$$

If $\eta < \eta^{\min}$ or $\eta > \eta^{\max}$, i.e., large negative or positive overpotentials, the potential difference across the surface double-layer can no longer be modified and, from Eqs. [14] and [16],

$$\begin{aligned} e\Delta\phi - e\Delta\phi_{O^{2-}} &= e\Delta\chi + e\Delta V_{\mathrm{lat},O^{2-}} \\ &= e\eta - \frac{1}{2}\Delta\mu_{O^{2-}} = \text{constant}. \end{aligned}$$

For $\eta < \eta^{\min}$,

$$e\eta - \frac{1}{2}\Delta\mu_{O^{2-}} \approx e\eta^{\min}, \tag{A3}$$

and for $\eta > \eta^{\max}$,

$$e\eta - \frac{1}{2}\Delta\mu_{O^{2-}} \approx e\eta^{\max}, \tag{A4}$$

with Eq. [A2] being obeyed,

$$\frac{\theta_*}{\theta_*^0} \approx \exp\left(-\frac{\Delta\mu_{O^{2-}}}{kT}\right).$$

For a negatively charged transition state,

$$r_- = r_9 + r_{12} + r_{15},$$

and at negative overpotentials Reaction 12 may dominate as a result of the reduced surface potential. Taking Eq. [39],

$$r_{12} = r_{12}^0 \frac{\theta_*}{\theta_*^0} \exp \frac{1}{kT}\left\{-\frac{a_{A^-B}}{a_{O^{2-}}}\left(e\eta - \frac{1}{2}\Delta\mu_{O^{2-}}\right)\right\},$$

and using Eqs. [23] and [A1] for intermediate oxygen-ion coverages,

$$r_{12} \approx r_{12}^0 \exp\left(-\frac{a_{A^-B}}{a_{O^{2-}}}\frac{e\eta}{kT}\right), \qquad \text{[A5]}$$

and evaluating the reaction rate, $r_{12}^{\min}$, at an overpotential of $\eta^{\min}$,

$$r_{12}^{\min} \approx r_{12}^0 \exp\left(-\frac{a_{A^-B}}{a_{O^{2-}}}\frac{e\eta^{\min}}{kT}\right).$$

At large negative overpotentials Eq. [A3] dictates that

$$e\eta - \frac{1}{2}\Delta\mu_{O^{2-}} \approx e\eta^{\min},$$

as it is no longer possible to modify the surface potential or the lateral interaction potential. The coverage of vacant sites remains constant and approximately equal to unity. This means that r_{12} can no longer be modified and

$$r_{12} \approx r_{12}^{\min}.$$

At positive overpotentials Reaction 15 may dominate as a result of electron donation from oxygen ions through Reaction 13. Using Eq. [45] with $\Delta\mu_O$ equal to zero,

$$r_{15} = r_{15}^0 \frac{\theta_*}{\theta_*^0} \exp \frac{1}{kT}\left\{\frac{1}{2}\Delta\mu_{O^{2-}} + \frac{a_{O^{2-}} - a_{AB^-}}{a_{O^{2-}}}\left(e\eta - \frac{1}{2}\Delta\mu_{O^{2-}}\right)\right\},$$

and using Eqs. [23] and [A1] for intermediate oxygen-ion coverages,

$$r_{15} \approx r_{15}^0 \exp\left(\frac{a_{O^{2-}} - a_{AB^-}}{a_{O^{2-}}}\frac{e\eta}{kT}\right), \qquad \text{[A6]}$$

and evaluating the reaction rate, $r_{15}^{\max}$, at an overpotential of $\eta^{\max}$,

$$r_{15}^{\max} \approx r_{15}^0 \exp\left(\frac{a_{O^{2-}} - a_{AB^-}}{a_{O^{2-}}}\frac{e\eta^{\max}}{kT}\right).$$

At large positive overpotentials Eq. [A4] dictates that

$$e\eta - \frac{1}{2}\Delta\mu_{O^{2-}} \approx e\eta^{\max},$$

as it is no longer possible to modify the surface potential or the lateral interaction potential and

$$r_{15} \approx r_{15}^{\max} \frac{\theta_*}{\theta_*^0} \exp\left(\frac{\Delta\mu_{O^{2-}}}{2kT}\right).$$

Using Eq. [A2] gives

$$r_{15} \approx r_{15}^{\max} \exp\left(-\frac{\Delta\mu_{O^{2-}}}{2kT}\right),$$

and

$$r_{15} \approx r_{15}^{\max} \exp\left\{\frac{1}{kT}(e\eta^{\max} - e\eta)\right\},$$

with the rate of Reaction 15 going through a maximum as the coverage of ionic oxygen approaches unity.

APPENDIX B: REACTION RATE AS A FUNCTION OF OVERPOTENTIAL FOR A POSITIVELY CHARGED TRANSITION STATE

For reactions involving positively charged transition states Reaction 25 may dominate at negative overpotentials as a result of electron donation to adsorbed oxygen through Reaction 23. Taking Eq. [51] with $\Delta\mu_O$ equal to zero,

$$r_{25} = r_{25}^0 \frac{\theta_*}{\theta_*^0} \exp \frac{1}{kT}\left\{-\frac{1}{2}\Delta\mu_{O^{2-}} - \frac{a_{O^{2-}} - a_{AB^+}}{a_{O^{2-}}} \times \left(e\eta - \frac{1}{2}\Delta\mu_{O^{2-}}\right)\right\},$$

and using Eqs. [23] and [A1] for intermediate oxygen-ion coverages,

$$r_{25} \approx r_{25}^0 \exp\left(-\frac{a_{O^{2-}} - a_{AB^+}}{a_{O^{2-}}}\frac{e\eta}{kT}\right), \qquad \text{[B1]}$$

and evaluating the reaction rate, $r_{25}^{\min}$, at an overpotential of $\eta^{\min}$,

$$r_{25}^{\min} \approx r_{25}^0 \exp\left(-\frac{a_{O^{2-}} - a_{AB^+}}{a_{O^{2-}}}\frac{e\eta^{\min}}{kT}\right).$$

At large negative overpotentials Eq. [A3] dictates that

$$\left(e\eta - \frac{1}{2}\Delta\mu_{O^{2-}}\right) \approx e\eta^{\min},$$

as it is no longer possible to modify the surface potential or the lateral interaction potential. The coverage of vacant sites remains constant and approximately equal to unity. Hence,

$$r_{25} \approx r_{25}^{\min} \exp\left(-\frac{\Delta\mu_{\mathrm{O}^{2-}}}{2kT}\right),$$

and

$$r_{25} \approx r_{25}^{\min} \exp\left\{\frac{1}{kT}(e\eta^{\min} - e\eta)\right\}.$$

At positive overpotentials Reaction 21 may dominate as a result of electron donation to the metal through Reaction 19. Taking Eq. [50],

$$r_{21} = r_{21}^{0}\frac{\theta_*}{\theta_*^0}\exp\frac{1}{kT}\left\{\frac{a_{\mathrm{A^+B}}}{a_{\mathrm{O}^{2-}}}\left(e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}}\right)\right\},$$

and using Eqs. [23] and [A1] for intermediate oxygen-ion coverages,

$$r_{21} \approx r_{21}^{0}\exp\left(\frac{a_{\mathrm{A^+B}}}{a_{\mathrm{O}^{2-}}}\frac{e\eta}{kT}\right), \qquad \text{[B2]}$$

and evaluating the reaction rate, $r_{21}^{\max}$, at an overpotential of $\eta^{\max}$,

$$r_{21}^{\max} \approx r_{21}^{0}\exp\left(\frac{a_{\mathrm{A^+B}}}{a_{\mathrm{O}^{2-}}}\frac{e\eta^{\max}}{kT}\right).$$

At large positive overpotentials Eq. [A4] dictates that

$$\left(e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}}\right) \approx e\eta^{\max},$$

as it is no longer possible to modify the surface potential or the lateral interaction potential; hence,

$$r_{21} \approx r_{21}^{\max}\frac{\theta_*}{\theta_*^0}.$$

Using Eq. [A2] gives

$$r_{21} \approx r_{21}^{\max}\exp\left(-\frac{\Delta\mu_{\mathrm{O}^{2-}}}{kT}\right),$$

and

$$r_{21} \approx r_{21}^{\max}\exp\left\{\frac{2}{kT}(e\eta^{\max} - e\eta)\right\}.$$

APPENDIX C: REACTIONS 1 AND 2 BOTH AT EQUILIBRIUM

In addition to Reaction 2 being at equilibrium it is interesting to consider what happens if Reaction 1 is also at equilibrium (therefore Reaction 3 must also be at equilibrium), i.e., Reactions 4 and 5 are slow. This means that we can no longer assume that the chemical potential of adsorbed neutral oxygen is constant as, using Eqs. [6] and [9],

$$e\eta = e\eta_{4/5} = \frac{1}{2}\Delta\mu_{\mathrm{O}}, \qquad \text{[C1]}$$

and the rate of reaction is modified by changing the virtual oxygen pressure associated with the catalyst surface (this has the same effect as modifying the gas-phase concentration of oxygen). The expressions we have derived for reaction rates as a function of overpotential are based on the surface chemical potentials of reactants being unmodified on polarisation. Therefore they are not valid if one of the reactants, A or B , is oxygen in the case of Reactions 4 and 5 being slow. However if oxygen is used solely to modify the catalyst properties, substituting Eq. [C1] into Eq. [39],

$$r_{12} = r_{12}^{0}\frac{\theta_*}{\theta_*^0}\exp\frac{1}{kT}\left\{-\frac{a_{\mathrm{A^-B}}}{a_{\mathrm{O}^{2-}}}\left(\frac{1}{2}\Delta\mu_{\mathrm{O}} - \frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}}\right)\right\},$$

and the reaction is slowed on increasing surface oxygen chemical potential because of the combination of a negatively charged transition state and an increased surface potential. If we look at the form of the rate expression for Reaction 15, substituting Eq. [C1] into Eq. [45],

$$\begin{aligned} r_{15} = r_{15}^{0}\frac{\theta_*}{\theta_*^0}\exp\frac{1}{kT}\bigg\{&\frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}} - \frac{1}{2}\Delta\mu_{\mathrm{O}} \\ &+ \frac{a_{\mathrm{O}^{2-}} - a_{\mathrm{AB}^-}}{a_{\mathrm{O}^{2-}}}\left(\frac{1}{2}\Delta\mu_{\mathrm{O}} - \frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}}\right)\bigg\} \\ r_{15} = r_{15}^{0}\frac{\theta_*}{\theta_*^0}\exp\frac{1}{kT}\bigg\{&-\frac{a_{\mathrm{AB}^-}}{a_{\mathrm{O}^{2-}}}\left(\frac{1}{2}\Delta\mu_{\mathrm{O}} - \frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}}\right)\bigg\}, \end{aligned}$$

and provided that the distance of the electron from the metal surface is the same for $\mathrm{A^-B}$ as $\mathrm{AB^-}$ then the change in the rate of Reaction 12 will be the same as the change in the rate of Reaction 15. This is a consequence of the equilibrium in Reactions 1, 2, and 3, meaning that electrons associated with the metal catalyst remain in equilibrium with electrons associated with the $\mathrm{O/O^{2-}}$ redox couple. Additionally such a system would exhibit clear limiting current behaviour as a result of the slow kinetics for Reactions 4 and 5.

NOMENCLATURE

Letters

a_i	Separation of dipole charges for the *i*th species
e	Charge on an electron
I	Current
I_i	Current associated with the *i*th reaction
I_0	Exchange current
$I_{0,i}$	Exchange current associated with the *i*th reaction

k	Boltzmann constant
k_i	Reaction rate constant for the ith reaction
K_i	Equilibrium constant for the ith reaction
N	Density of surface sites
r	Area specific reaction rate
$r_{O^{2-}}$	Effective ionic radius of a surface oxygen ion
r_i	Area specific reaction rate for the ith reaction
r_-	Area specific reaction rate for and electrophilic reaction
r_+	Area specific reaction rate for and electrophobic reaction
R	Reaction rate
S_{ct}	Selectivity for oxygen ion formation as a result of charge transfer
S_{surf}	Selectivity for oxygen ion formation as a result of oxygen adsorption
$V_{lat,i}$	Potential associated with lateral dipole–dipole interactions between an adsorbed ion (and hence dipole) of the ith species and the adsorbed oxygen ions

Greek Letters

α	A constant used in Eq. (3)
χ	Surface potential
ε_0	Vacuum permittivity
ϕ	Potential
ϕ_i	Potential of electrons associated with the ith species
Φ	Extraction potential
Φ^*	Threshold extraction potential
η	Overpotential
η_i	Activation overpotential associated with ith reaction
η^*	Threshold overpotential
Λ	Enhancement factor
μ	Dipole moment of a doubly charged oxygen ion
μ_i	Chemical potential of the ith species
$\bar{\mu}_i$	Electrochemical potential of the ith species
σ	Charge density
θ_i	Fractional coverage of the ith species
Ψ	Outer potential

Superscripts

0	Unpolarised condition
max	Maximum value, except for overpotential when it refers to the overpotential associated with the approach to maximum in surface potential
min	Minimum value, except for overpotential when it refers to the overpotential associated with the approach to minimum in surface potential

Subscripts

ct	Associated with charge transfer
supp	Associated with the catalyst support
surf	Associated with the catalyst surface

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