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Electrochemical Promotion of Catalysis

I: Thermodynamic Considerations

Ian S. Metcalfe[1]

School of Chemical Engineering, University of Edinburgh, Edinburgh EH9 3JL, Scotland, United Kingdom

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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 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 this basis thermodynamic relationships governing the chemical potentials of the catalyst surface oxygen species are derived for the case of a pure ion-conducting support with fast surface and gas-phase diffusion of species. It is shown that, in the case of very stable oxygen ions, the application of a moderate overpotential to the catalyst/support interface results in a change in the catalyst surface potential equal to the applied overpotential provided that lateral interactions between oxygen ions can be neglected.

1. INTRODUCTION

In recent years the importance of spillover processes in catalysis has been widely acknowledged. Delmon and Froment in particular have promoted the idea of “remote control” (1) in catalysis where an inert support phase may donate spillover species to an active catalytic phase. In this manner the selectivity and activity of the catalytic phase may be “controlled” by the support. More specifically, 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 small currents of 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 (2–4)) 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-ion conductors (16). Electrochemical promotion has also been observed in the case of a titania mixed ionic-conducting and electronic-conducting support (17). 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)

$$\eta = \Delta\Phi, \tag{1}$$

where η is the applied overpotential and $\Delta\Phi$ is the change in electron extraction potential of the catalyst. Any imposed overpotential is reflected by a change in the macroscopically determined work function (determined with a Kelvin probe and equal to $e\Delta\Phi$ where e is the charge on an electron). 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. This change in work function modifies the kinetic behaviour of the catalyst and, in general, the new reaction rate, R, can be related to the overpotential by an equation of the form (e.g. 2)

$$\ln\frac{R}{R^0} = \alpha\frac{e(\Delta\Phi - \Delta\Phi^*)}{kT}, \tag{2}$$

where k is the Boltzmann constant, R^0 is the open-circuit reaction rate, and α and $\Delta\Phi^*$ are empirically determined constants.

In other work Metcalfe and co-workers (18–20) have studied the behaviour of a platinum electrode both in air and under reaction conditions. They found that the change in electron extraction potential was related to the overpotential (within the range of investigation); however, the two were not equal,

$$\Delta\Phi = \xi\eta, \tag{3}$$

where ξ depends upon operating conditions and electrode morphology. As with the work of Vayenas, reaction rate

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[1] Present Address: Department of Chemical Engineering, UMIST, P.O. Box 88, Manchester M60 1QD, United Kingdom. Fax: +44 161 200 4399. E-mail: ian.metcalfe@umist.ac.uk.

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modifications were observed and obeyed Eq. [2]. ξ was found to decrease as the atmosphere became more reducing and also to decrease as the gas–electrode interfacial surface area was increased relative to the length of electrode–electrolyte–gas three-phase boundary. This was explained in terms of the finite reactivity and surface diffusivity of the ionic spillover species responsible for changes in extraction potential and reaction rate. (Later, recent work by the group of Vayenas has also recognised the significance of low rates of surface diffusion of spillover species (21).) Only in the case of low reactivity of the spillover species with fast surface diffusion, would Eq. [1] be expected to hold. It should be noted that therefore, in general, the extraction potential need not be constant but will vary spatially. Hence both reaction rate and measured extraction potential change will depend upon an average extraction potential change; however, this averaging is performed differently in each case.

Imbihl *et al.* (22) investigated the variation of extraction potential with applied overpotential for electrodes prepared in their own laboratory and electrodes prepared in the laboratory of Vayenas and co-workers in Patras. They did indeed find Eq. [1] to be valid for the Patras electrodes but found that their own electrodes showed no change in extraction potential under similar conditions. This was attributed to spillover species remaining close to the three-phase boundary line and not spilling over the entire catalyst surface (an explanation consistent with that of Metcalfe *et al.* (18–20)). However, work using photoelectron emission microscopy (PEEM) to measure dynamic work function changes on NEMCA-active electrodes with a resolution of 1 μm (23) was unable to resolve work function fronts spreading across the catalyst surface as expected. X-ray photoelctron spectroscopy indicated the nature of the oxygen spillover species (24) to be the same as chemisorbed oxygen from the gas phase. Imbihl *et al.* have also recently (25) attempted to use simple thermodynamic arguments to comment on the origin and validity of Eq. [1].

The purpose of this paper is to derive from first principles a framework for understanding and interpreting catalytic behaviour in the presence of ionic spillover from a support to a metal catalyst. As an example, a metal supported on an oxygen-ion-conducting support will be considered. However, the approach developed here could equally be applied to other support materials. In particular the area of electrochemical promotion will be addressed.

2. THE CLEAN METAL SURFACE

Let us consider a working electrochemical cell. The electrochemical potential of electrons associated with an electrode, $\bar{\mu}_e$, can be related to the inner or Galvani potential of the electrode, ϕ, and the chemical potential of the electrons, μ_e (see Fig. 1),

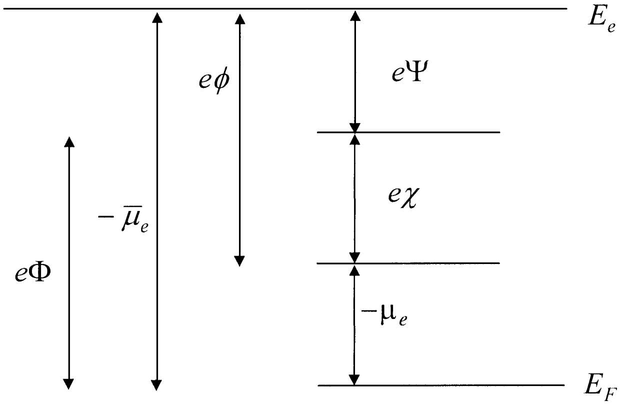

FIG. 1. Energy levels at a metal surface relative to the energy of a free electron, E_e.

$$\bar{\mu}_e = \mu_e - e\phi. \quad [4]$$

This potential can be split into a surface potential, χ, and an outer potential or Volta potential, Ψ,

$$\phi = \chi + \Psi. \quad [5]$$

Substituting Eq. [5] into Eq. [4],

$$\bar{\mu}_e = \mu_e - e\chi - e\Psi. \quad [6]$$

Using the definition of work function, $e\Phi$, where Φ is the electron extraction potential,

$$e\Phi = -\mu_e + e\chi, \quad [7]$$

and substituting into Eq. [6],

$$\bar{\mu}_e = -e\Phi - e\Psi. \quad [8]$$

It should be noted that the work function is not uniform over a catalyst surface but will be different on different crystal faces. Indeed a rough surface will have a lower work function than a smooth surface because of the orientation of surface dipoles. Consequently, as the electrochemical potential of electrons in a metal catalyst must be uniform, spatial variations in work function result in spatial variations in outer potential in accordance with Eq. [8].

3. THE METAL SURFACE IN THE PRESENCE OF AN ADSORBATE

If an adsorbate, such as oxygen, is introduced onto the metal surface, electron exchange between the metal and adsorbate may occur (here we will confine our discussion to oxygen but we could alternatively describe the influence of an alkali metal promoter such as sodium in the same manner). As oxygen is electrophilic, there will be a tendency for electrons to be donated from the metal to the surface oxygen. Here, for the purposes of illustration, we will consider only two adsorbed oxygen species, neutral O atoms and O^{2-} oxygen ions, to have significant coverages. Furthermore, we consider the coverage of all other ions to be insignificant compared to the coverage of oxygen ions such that the properties of the surface double layer are dictated by the presence of the oxygen ions alone. (This is simplistic as we may expect more forms of ionic oxygen, as well as ions associated with coadsorbates, to be present. The approach used here is general and can accommodate more species if necessary.) If the chemical potential of surface oxygen is fixed by equilibrium with the gas phase,

$$\frac{1}{2}\mu_{\mathrm{O}} = \frac{1}{4}\mu_{\mathrm{O}_2}, \qquad [9]$$

the electrochemical potential of ionic forms of surface oxygen will be fixed at equilibrium,

$$\frac{1}{2}\bar{\mu}_{\mathrm{O}^{2-}} = \frac{1}{2}\mu_{\mathrm{O}} + \bar{\mu}_e = \frac{1}{4}\mu_{\mathrm{O}_2} + \bar{\mu}_{\mathrm{e}}, \qquad [10]$$

where the electrochemical potential of electrons associated with the bulk of the metal is given by Eq. [4]. Remembering that the oxygen ions reside on the surface of the catalyst we can relate their electrochemical potential and chemical potential. Let the potential of electrons associated with the oxygen ions be ϕ_{O}^{2-}, then

$$\frac{1}{2}\bar{\mu}_{\mathrm{O}^{2-}} = \frac{1}{2}\mu_{\mathrm{O}^{2-}} - e\phi_{\mathrm{O}^{2-}}. \qquad [11]$$

Combining the above with Eqs. [4] and [10] gives

$$\frac{1}{2}\mu_{\mathrm{O}^{2-}} = \frac{1}{2}\mu_{\mathrm{O}} + \mu_{\mathrm{e}} - e\phi + e\phi_{\mathrm{O}^{2-}}. \qquad [12]$$

The energy required to remove an electron from the metal and hold it on the surface in the form of an oxygen ion depends upon the surface potential barrier, χ, and any lateral interactions between the ions (or more correctly dipoles), $V_{\mathrm{lat,O}^{2-}}$. We can relate the potential of electrons associated with the metal to the potential of electrons associated with the oxygen ions,

$$\phi = \phi_{\mathrm{O}^{2-}} + \chi + V_{\mathrm{lat,O}^{2-}}, \qquad [13]$$

provided that electrons must cross the entire surface potential barrier on creation or destruction of an O^{2-} ion (this is true if O^{2-} ions are the only ions present in significant amounts). Note that combining Eqs. [5] and [13] gives

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

and in the absence of lateral interactions the outer potential is equal to the potential of the electrons associated with the oxygen ions.

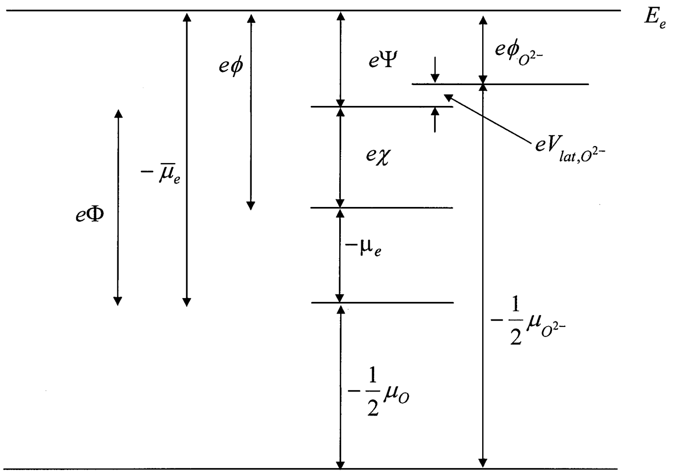

FIG. 2. Energy levels at a metal surface in the presence of oxygen as an adsorbate at equilibrium.

Figure 1 can be extended to show the equilibria associated with adsorbed oxygen species (see Fig. 2).

Substituting Eq. [13] into Eq. [11],

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

Combining with Eqs. [4] and [10],

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

Equation [16] can be written in terms of differences, remembering that the chemical potential of electrons associated with the metal remains constant,

$$\frac{1}{2}\Delta\mu_{\mathrm{O}^{2-}} + e\Delta\chi + e\Delta V_{\mathrm{lat,O}^{2-}} = \frac{1}{2}\Delta\mu_{\mathrm{O}}. \qquad [17]$$

To proceed further we need to investigate how each of the terms of the left-hand side of Eq. [17] depend on the coverage of oxygen ions.

For a Langmuir adsorption isotherm (i.e., no lateral interactions and similar energetics for all sites), it can easily be shown that

$$\mu_{\mathrm{O}} = \mu_{\mathrm{O}}^{\theta} + kT\ln\frac{\theta_{\mathrm{O}}}{\theta_*}\frac{\theta_*^{\ominus}}{\theta_{\mathrm{O}}^{\theta}}, \qquad [18]$$

with the superscript $\ominus$ referring to a standard state and θ_* being the coverage of vacant sites. Furthermore,

$$\mu_{\mathrm{O}}^{\ominus} = \frac{\Delta G^{\ominus}}{2},$$

where $\Delta G^{\ominus}$ is the free energy of chemisorption per molecule of oxygen. With the standard state defined as having equal coverages of occupied and unoccupied sites,

$$\mu_{\mathrm{O}} = \mu_{\mathrm{O}}^{\ominus} + kT \ln \frac{\theta_{\mathrm{O}}}{\theta_*}. \qquad [19]$$

Using the Fermi distribution function (see Appendix A), we can show that the chemical potential of oxygen ions is given by

$$\mu_{\mathrm{O}^{2-}} = \mu_{\mathrm{O}^{2-}}^{\ominus} + kT \ln \frac{\theta_{\mathrm{O}^{2-}}}{\theta_*}. \qquad [20]$$

Hence,

$$\Delta\mu_{\mathrm{O}^{2-}} = kT \ln \frac{\theta_{\mathrm{O}^{2-}}}{\theta_*} \frac{\theta_*^0}{\theta_{\mathrm{O}^{2-}}^0}, \qquad [21]$$

where the superscript 0 is used to represent an initial catalyst state.

We may express changes in the surface potential in terms of changes in ionic coverage through the Helmholtz equation. As doubly charged oxygen ions are the only ions with any appreciable coverage,

$$e\Delta\chi = \frac{(\sigma - \sigma^0)\mu}{2\varepsilon_0} = \frac{Ne\mu\left(\theta_{\mathrm{O}^{2-}} - \theta_{\mathrm{O}^{2-}}^0\right)}{\varepsilon_0}, \qquad [22]$$

where N is the density of surface sites, σ is the surface charge density, ε_0 is the vacuum permittivity, and μ is the dipole moment of the oxygen ion. Obviously the coverage of neutral oxygen atoms does not appear in the above expression because of a zero dipole moment (oxygen adsorption increases surface potential as a result of increasing the oxygen-ion coverage).

We take account of the potential energy of an ion (or more correctly a dipole when the image charge is included) as a result of lateral interaction with all other surface ions or dipoles. By considering a hexagonal array of oxygen ions, with $a_{\mathrm{O}^{2-}}$ being the separation distance of the dipole charges for the oxygen ion and $r_{\mathrm{O}^{2-}}$ being the effective ionic radius of the oxygen ion, we can show from simple electrostatic arguments (see Appendix B) that the lateral interaction potential between ions is given by

$$V_{\mathrm{lat,O}^{2-}} = \frac{N\mu}{\varepsilon_0} \frac{\pi\sqrt{3}}{16} \frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}} \theta_{\mathrm{O}^{2-}}^{3/2}. \qquad [23]$$

Hence,

$$e\Delta V_{\mathrm{lat,O}^{2-}} = \frac{Ne\mu}{\varepsilon_0} \frac{\pi\sqrt{3}}{16} \frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}} \left(\theta_{\mathrm{O}^{2-}}^{3/2} - \theta_{\mathrm{O}^{2-}}^{0\;3/2}\right). \qquad [24]$$

If we return to Eq. [17],

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

substitution of Eqs. [21], [22], and [24] above yields a differential form of the oxygen-ion adsorption isotherm; we know how each of the terms on the left-hand side of the equation depend on oxygen-ion coverage. Provided that ionic oxygen is not completely absent from the surface, and neither is the surface coverage of ionic oxygen so high as to approach limiting coverages, and given that

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

we may neglect the logarithmic terms in $\theta_{\mathrm{O}^{2-}}$ which appear in the expression for the change in chemical potential of oxygen ions (Eq. [21]) in comparison with the surface potential barrier (Eq. [22]) and lateral interaction terms (Eq. [24]) which have a stronger dependence on $\theta_{\mathrm{O}^{2-}}$. (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,

$$\Delta\mu_{\mathrm{O}^{2-}} \approx 0, \qquad [25]$$

and

$$e\Delta\chi + e\Delta V_{\mathrm{lat,O}^{2-}} \approx \frac{1}{2}\Delta\mu_{\mathrm{O}}. \qquad [26]$$

In the absence of lateral interactions, Eq. [26] becomes

$$e\Delta\chi \approx \frac{1}{2}\Delta\mu_{\mathrm{O}}. \qquad [27]$$

Consequently, increasing oxygen chemical potential will increase the work function, while decreasing oxygen chemical potential will decrease the work function as expected. In addition, Eq. [25] shows that the oxygen-ion coverage is severely limited as a result of the presence of a surface double layer (the Weisz limitation).

4. THE METAL/ION-CONDUCTING SUPPORT INTERFACE

Now consider a metal in contact with an oxygen-ion-conducting support (again the arguments presented here could also be applied to any other ion-conducting support such as a sodium-ion-conducting support) in the presence of an oxygen/inert atmosphere and under open-circuit conditions. The oxygen ions of the support (here denoted $\mathrm{O}^{2-}_{\mathrm{supp}}$) will equilibrate with the adsorbed oxygen and electrons associated with the catalyst,

$$\mathrm{O}^{2-}_{\mathrm{supp.}} \Leftrightarrow \mathrm{O} + 2e^-, \qquad [\text{Reaction } 1]$$

and indeed all other forms of oxygen on the catalyst surface through parallel charge transfer reactions,

$$\mathrm{O}^{2-}_{\mathrm{supp.}} \Leftrightarrow \mathrm{O}^{2-}. \qquad [\text{Reaction } 2]$$

It should be noted that the charge-transfer reactions do not need to be responsible for introducing a new form of surface ionic oxygen. Rather, all forms of surface oxygen are present on the surface of the metal even in the absence of the ion-conducting support provided that equilibrium is achieved.

At equilibrium electrochemical potentials can be equated for the two charge-transfer reactions,

$$\frac{1}{2}\bar{\mu}_{\mathrm{O^{2-},supp}} = \frac{1}{2}\mu_{\mathrm{O}} + \bar{\mu}_{\mathrm{e}} \qquad [28]$$

$$\frac{1}{2}\bar{\mu}_{\mathrm{O^{2-},supp}} = \frac{1}{2}\bar{\mu}_{\mathrm{O^{2-}}}. \qquad [29]$$

This equilibrium would also exist for any other forms of ionic oxygen present and there will also be equilibrium between electrons associated with the support and those associated with the catalyst as a result of an additional charge-transfer reaction involving only electrons,

$$\bar{\mu}_{\mathrm{e,supp}} = \bar{\mu}_{\mathrm{e}}. \qquad [30]$$

We can now modify Fig. 2 (see Fig. 3) to show the presence of the oxygen-ion-conducting support and the equilibrium of the charge-transfer reactions, Reactions 1 and 2.

The reactions involving oxygen can be described by a simple reaction network (see Fig. 4). Reactions 1 and 2 are the two previously referred-to 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.

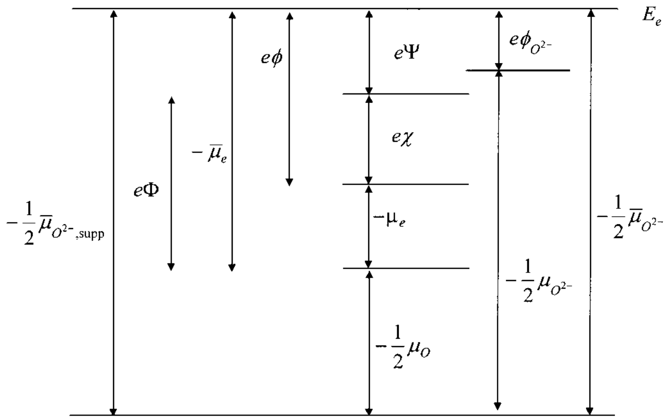

FIG. 3. Energy levels at a metal surface in the presence of oxygen as an adsorbate and in contact with an oxygen-ion-conducting support at equilibrium.

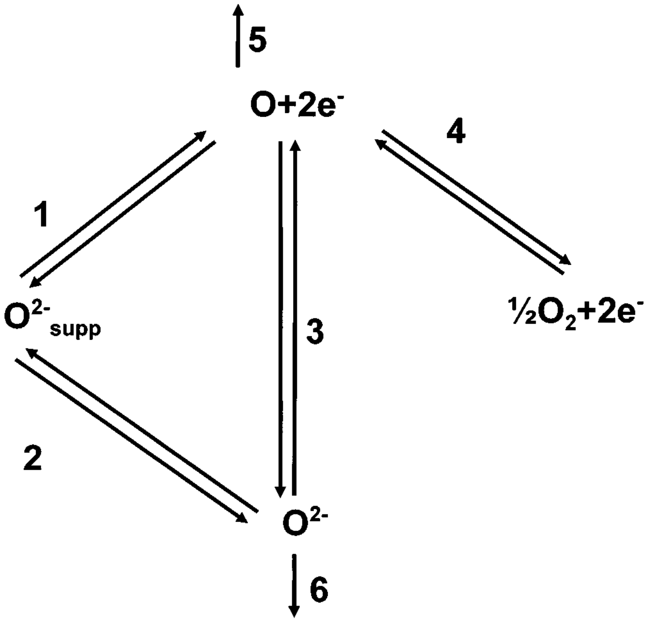

FIG. 4. Reaction network for oxygen species associated with a metal supported on an oxygen-ion conductor. The support surface is assumed to be inert.

The arguments can be now extended for the case of a reactive system where there need no longer be equilibria between oxygen on the catalyst surface and oxygen in the gas phase and between different forms of oxygen on the surface of the catalyst. Under reaction conditions, achieved for example by the addition of a reducing gas to the oxygen in the gas phase, we assume an inert support surface and we do not allow the reducing gas to participate in any charge-transfer reactions. Reactions 5 and 6 are now included in Fig. 4 and involve the removal of surface oxygen and surface ionic oxygen respectively by reaction with the reducing gas. At steady state the chemical potential of adsorbed oxygen species (which will be different on differing surfaces because of differences in reactivities) must be less than or equal to that of gas-phase molecular oxygen,

$$\frac{1}{2}\mu_{\mathrm{O}} \le \frac{1}{4}\mu_{\mathrm{O_2}}.$$

Likewise, the electrochemical potential of the ionic oxygen species must be less than that which would be in equilibrium with the adsorbed oxygen,

$$\frac{1}{2}\bar{\mu}_{\mathrm{O^{2-}}} \le \frac{1}{2}\mu_{\mathrm{O}} + \bar{\mu}_{\mathrm{e}}.$$

As oxidation and reduction of the support cannot take place through the support surface alone because of its inert nature, the electrochemical potential of the support ionic oxygen must lie between these two extremes,

$$\frac{1}{2}\bar{\mu}_{\mathrm{O^{2-}}} \le \frac{1}{2}\bar{\mu}_{\mathrm{O^{2-},supp}} \le \frac{1}{2}\mu_{\mathrm{O}} + \bar{\mu}_{\mathrm{e}}.$$

Therefore, because of the reactivity of the surface ionic oxygen species there can be, at steady state, a consumption of adsorbed oxygen to produce adsorbed ionic oxygen through both the reverse of Reaction 3 and the reverse of Reaction 1 and forward Reaction 2 in series. This of course means that although the system is under open-circuit conditions the charge-transfer reactions do not need to be at equilibrium under reaction conditions (rather an effect

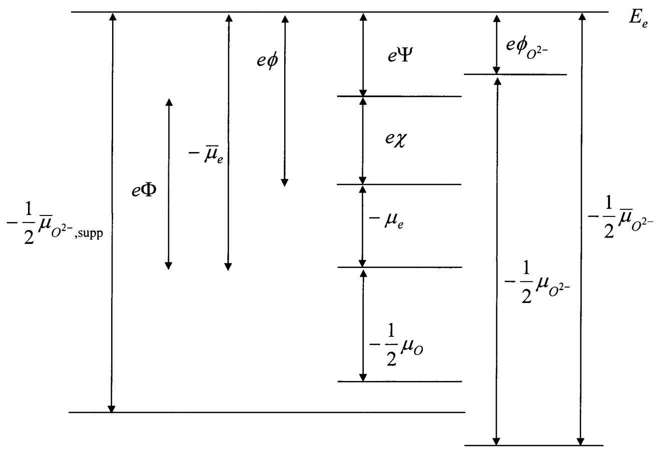

FIG. 5. Energy levels at a metal surface in contact with an oxygen-ion-conducting support showing how lack of equilibrium between adsorbed oxygen and adsorbed ionic oxygen can lead to a corrosion current.

similar to a corrosion current can occur resulting in the production of ionic oxygen). Figure 5 illustrates the energies associated with this particular case. In Fig. 5 we can see that there is a driving force for the reverse of Reaction 1, i.e., electronation of surface oxygen resulting in the formation of an oxygen ion in the support. There is also a driving force for the forward Reaction 2 resulting in the formation of surface oxygen ions from support oxygen ions. Therefore, we would not expect a metal catalyst supported on an oxygen-ion conductor to behave in the same manner as the unsupported metal as, even under open-circuit conditions, interfacial reactions will modify the coverages of adsorbates.

To allow future energy diagrams to remain clear, we will assume that under open-circuit conditions Reactions 1 and 2, and hence Reaction 3, are not polarised, i.e., there is no corrosion-like current resulting in continuous spillover of ionic oxygen in the catalyst/support interfacial region. The energetics of the open-circuit case are therefore represented by Fig. 3 and not Fig. 5. This situation would occur if the ionic oxygen is of low reactivity, i.e., it does not easily react with any reducing gases present through Reaction 6 (indeed later we also need to invoke a low reactivity to explain the validity of Eq. [1]) and therefore equilibrates with ionic oxygen in the support as well as adsorbed neutral oxygen.

5. SOLID–ELECTROLYTE SUPPORT AND POLARISATION OF THE METAL/ION CONDUCTOR INTERFACE

We now form an electrochemical cell consisting of two metal electrodes separated by the ion conductor. Provided that the electronic conductivity of the ion conductor is very low compared to the ionic conductivity then the electrochemical potential of oxygen ions will remain uniform within the support when both electrodes are exposed to different conditions. Furthermore, the low electronic conductivity will mean that only a small flux of electrons, and hence oxygen ions, crosses the membrane under open-circuit conditions. Therefore Reactions 1 and 2 will be at equilibrium. The above conditions are satisfied by solid–electrolyte supports and we will hence confine our discussions to these materials. (Note that Reactions 1 and 2 can only be in equilibrium across the entire electrode/electrolyte interface if chemical potentials at the interface are uniform. Under reaction conditions this is achievable in a gradientless reactor.)

Provided that the assumptions behind Eq. [25] hold, the chemical potential of oxygen ions on the two electrodes will be approximately the same. As a result of the electrochemical potential of oxygen ions in the support being uniform, under open-circuit conditions the potential of electrons associated with surface ionic oxygen must be the same for both electrodes (i.e., the outer potential is fixed in the absence of lateral interactions). Consequently the emf of the cell will depend upon the potential differences across the gas-exposed electrode surface double layers and, hence, in the absence of lateral interactions, the emf will depend upon the surface potentials of the two electrodes as has previously been suggested by Vayenas *et al.* (2) as a result of experimental work.

We have already argued that, in general, we must consider at least two charge-transfer reactions between the adsorbed oxygen species and the oxygen-ion-conducting support. However, there is also indirect experimental evidence that there must be at least two parallel charge-transfer reactions occurring in the case of solid–electrolyte supports. We may argue that for the metal work function to be modified the coverage of at least one form of oxygen must be modified significantly. If there is a single charge-transfer process, modification of a surface coverage would mean the occurrence of limiting currents. However, electrodes are known to exhibit rate modification in the absence of limiting currents and under conditions where the Butler–Volmer equation is obeyed (2). In addition, although modification of the coverage of an ionic species is required for a change in the catalyst surface potential, Imbihl *et al.* (24) have only observed changes in the coverage of an oxygen species (not necessarily ionic) similar to those species formed by oxygen chemisorption from the gas phase. It is possible that a second charge-transfer reaction is occurring which results in a change in the coverage of a more ionic species (this change would be limited by the Weisz limitation) undetected by the X-ray photoelectron spectroscopy because of the other strong oxygen signal. Therefore we may expect at least two parallel charge-transfer reactions.

On polarisation the potential of the metal is instantaneously (on the time scale of spillover and reaction effects) modified. If the potential of the electrode is measured relative to the potential of a fixed-potential reference electrode, then

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

where the superscript 0 is now used to signify the initial unpolarised value of the metal potential and η is the overpotential. (If the oxygen-ion conductivity is low it may be necessary to allow for resistive losses in the electrolyte. Although this affects the way in which overpotential is measured it does not affect the analysis presented below.) From Eqs. [4] and [8], and remembering that the chemical potentials of electrons will be unchanged,

$$e\eta = e(\phi - \phi^0) = -\bar{\mu}_\mathrm{e} + \bar{\mu}_\mathrm{e}^0 = e(\Phi - \Phi^0) + e(\Psi - \Psi^0),$$

or

$$\eta = \Delta\Phi + \Delta\Psi = \Delta\chi + \Delta\Psi. \qquad [31]$$

However, instantaneously, the surface potential cannot be modified as there is no possibility of instantaneous spillover,

$$\Delta\chi^\mathrm{i} = \chi^\mathrm{i} - \chi^0 = 0,$$

where the superscript i refers to the instantaneous value of the variable immediately after polarisation. Surface coverages remain unchanged, with

$$\eta = \Delta\Psi^\mathrm{i} = \Psi^\mathrm{i} - \Psi^0.$$

The energetics immediately after polarisation (and before spillover has occurred) are shown in Fig. 6 (note that the use of a fixed-potential reference electrode exposed to a constant oxygen chemical potential means that for a fast oxygen-ion conductor with negligible resistive losses the electrochemical potential of oxygen ions in the support electrolyte is both uniform and fixed). In addition we consider the case of the working electrode being exposed to constant chemical potentials of gas-phase species, i.e., any reaction rate changes are small or the reactor is operated differentially. This imposed change in outer potential results in a driving force for oxygen migration between the YSZ electrolyte and the three-phase boundary (tpb) where either of the two charge-transfer reactions may take place. Oxygen supplied electrochemically from the support may form either adsorbed oxygen or adsorbed ionic oxygen. Initially the activation overpotentials for these two reactions are equal and equal to the electrode overpotential,

$$\eta = \eta_1^\mathrm{i} = \eta_2^\mathrm{i}.$$

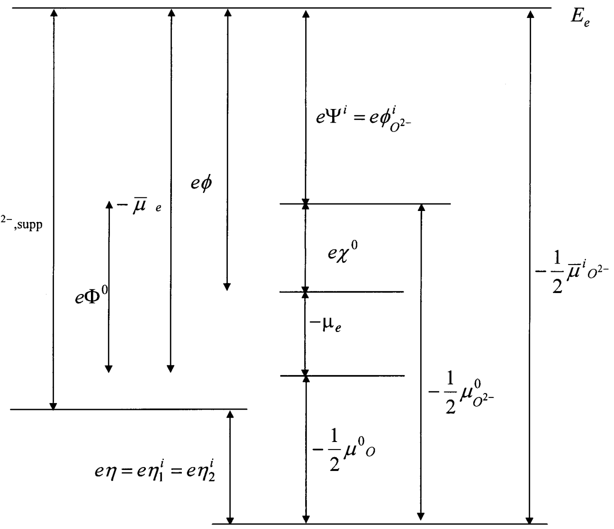

FIG. 6. Energy levels at a metal surface in contact with an oxygen-ion-conducting solid electrolyte immediately after polarisation. For clarity lateral dipole–dipole interactions are neglected. The reference electrode (not shown) is held at a fixed potential and resistive losses in the electrolyte are considered to be negligible.

Both the ionic oxygen species created by Reaction 2, and the neutral oxygen species created by Reaction 1, spill over the catalyst surface. The ionic species in turn can decompose to form adsorbed oxygen species. As spillover onto the catalyst surface takes place, the chemical potentials of the adsorbed species may be modified. This results in the formation of concentration overpotentials which will, in general, be different for the different charge-transferreactions.

It is possible to separate the overpotential into individual contributions due to the activation overpotential for the charge-transfer reaction, η_1 or η_2, an overpotential due to the kinetics of surface diffusion of the oxygen species involved in the charge-transfer reaction, $\eta_{\mathrm{sd,O}}$ or $\eta_{\mathrm{sd,O^{2-}}}$, an overpotential due to the finite rate of the decomposition of surface ionic oxygen into surface oxygen, η_3, an overpotential as a result of the kinetics of oxygen adsorption and desorption (Reaction 4) and removal through Reaction 5, $\eta_{4/5}$, and an overpotential due to the finite rate of oxygen diffusion in the gas phase, $\eta_{\mathrm{d,O_2}}$. By inspection of Fig. 4,

$$\eta = \eta_1 + \eta_{\mathrm{sd,O}} + \eta_{4/5} + \eta_{\mathrm{d,O_2}}$$
$$\eta = \eta_2 + \eta_{\mathrm{sd,O^{2-}}} + \eta_3 + \eta'_{\mathrm{sd,O}} + \eta_{4/5} + n'_{\mathrm{d,O_2}},$$

where $\eta'_{\mathrm{sd,O}}$ and $\eta'_{\mathrm{d,O_2}}$ are not necessarily equal to $\eta_{\mathrm{sd,O}}$ and $\eta_{\mathrm{d,O_2}}$ as different length scales may be involved in the two different overall charge-transfer processes. We will assume that gas-phase diffusion is fast and hence we get

$$\eta = \eta_1 + \eta_{\mathrm{sd,O}} + \eta_{4/5}$$
$$\eta = \eta_2 + \eta_{\mathrm{sd,O^{2-}}} + \eta_3 + \eta'_{\mathrm{sd,O}} + \eta_{4/5}.$$

$\eta_{\mathrm{sd,O}}$, $\eta_{\mathrm{sd,O^{2-}}}$, η_3, and $\eta_{4/5}$ will vary over the catalyst surface with $\eta_{\mathrm{sd,O}}$ and $\eta_{\mathrm{sd,O^{2-}}}$ approaching zero close to the three-phase boundary and η_3 and $\eta_{4/5}$ approaching zero at infinite distances from the three-phase boundary where concentrations of adsorbed species cannot be modified.

Here let us ignore any spatial variations in coverages, i.e., we assume fast surface diffusion of all species and set $\eta_{\mathrm{sd,O}}$

and $\eta_{\mathrm{sd,O^{2-}}}$ equal to zero and therefore η_3 and $\eta_{4/5}$ will take the same value at every point on the catalyst surface,

$$\eta = \eta_1 + \eta_{4/5} = \eta_2 + \eta_3 + \eta_{4/5}. \qquad [32]$$

Before polarisation, restating our assumption that both charge-transfer reactions are at equilibrium, i.e., no net conversion of one form of surface oxygen into the other form through these reactions, then we can use Eqs. [28] and [29],

$$\frac{1}{2}\bar{\mu}^0_{\mathrm{O^{2-}_{supp}}} = \frac{1}{2}\mu^0_{\mathrm{O}} + \bar{\mu}^0_{\mathrm{e}} \qquad [33]$$

$$\frac{1}{2}\bar{\mu}^0_{\mathrm{O^{2-}_{supp}}} = \frac{1}{2}\bar{\mu}^0_{\mathrm{O^{2-}}}. \qquad [34]$$

At any time after polarisation these equations no longer hold as there is no charge-transfer equilibrium and they should be modified to show the influence of the relevant activation overpotentials,

$$\frac{1}{2}\bar{\mu}_{\mathrm{O^{2-}_{supp}}} = \frac{1}{2}\mu_{\mathrm{O}} + \bar{\mu}_{\mathrm{e}} + e\eta_1 \qquad [35]$$

$$\frac{1}{2}\bar{\mu}_{\mathrm{O^{2-}_{supp}}} = \frac{1}{2}\bar{\mu}_{\mathrm{O^{2-}}} + e\eta_2. \qquad [36]$$

(Note that Eqs. [34] and [36] are valid at all locations on the catalyst surface provided that the chemical potential of adsorbed ionic oxygen is uniform, i.e., oxygen-ion surface diffusion alone is fast. Fast surface diffusion of neutral oxygen and fast gas-phase diffusion are not required.)

As the electrochemical potential of oxygen ions associated with the support is constant when using a fixed-potential reference electrode, Eqs. [33] and [34] can be used to eliminate the electrochemical potential of oxygen ions in the support to give

$$e\eta_1 = \left(\frac{1}{2}\mu^0_{\mathrm{O}} + \bar{\mu}^0_{\mathrm{e}}\right) - \left(\frac{1}{2}\mu_{\mathrm{O}} + \bar{\mu}_e\right)$$

$$e\eta_2 = \frac{1}{2}\bar{\mu}^0_{\mathrm{O^{2-}}} - \frac{1}{2}\bar{\mu}_{\mathrm{O^{2-}}}.$$

Substituting for electrochemical potentials,

$$e\eta_1 = \left(\frac{1}{2}\mu^0_{\mathrm{O}} + \mu^0_{\mathrm{e}} - e\phi^0\right) - \left(\frac{1}{2}\mu_{\mathrm{O}} + \mu_{\mathrm{e}} - e\phi\right)$$

$$e\eta_2 = \left(\frac{1}{2}\mu^0_{\mathrm{O^{2-}}} - e\phi^0_{\mathrm{O^{2-}}}\right) - \left(\frac{1}{2}\mu_{\mathrm{O^{2-}}} - e\phi_{\mathrm{O^{2-}}}\right).$$

Recalling Eq. [13],

$$\phi = \phi_{\mathrm{O^{2-}}} + \chi + V_{\mathrm{lat,O^{2-}}}$$

$$e\eta_2 = \left(\frac{1}{2}\mu^0_{\mathrm{O^{2-}}} - e\phi^0 + \chi^0 + V^0_{\mathrm{lat,O^{2-}}}\right) - \left(\frac{1}{2}\mu_{\mathrm{O^{2-}}} - e\phi + \chi + V_{\mathrm{lat,O^{2-}}}\right).$$

The chemical potential of the electrons is constant so we can conveniently rewrite these equations in terms of differences,

$$e\eta_1 = e\eta - \frac{1}{2}\Delta\mu_{\mathrm{O}} \qquad [37]$$

$$e\eta_2 = e\eta - e\Delta\chi - e\Delta V_{\mathrm{lat,O^{2-}}} - \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}}. \qquad [38]$$

Equation [32] gives

$$e\eta_3 = e\eta_1 - e\eta_2,$$

and therefore, using Eqs. [37] and [38],

$$e\eta_3 = e\Delta\chi + e\Delta V_{\mathrm{lat,O^{2-}}} + \frac{1}{2}\Delta\mu_{\mathrm{O^{2-}}} - \frac{1}{2}\Delta\mu_{\mathrm{O}}. \qquad [39]$$

Equations [32] and [37] give

$$e\eta_{4/5} = \frac{1}{2}\Delta\mu_{\mathrm{O}}. \qquad [40]$$

The energetics corresponding to the above equations are shown in Fig. 7. The network with the appropriate driving forces is illustrated Fig. 8.

Therefore in general the coverage of O^{2-} will be kinetically determined, although it may be true that if such a species is relatively stable then for appropriate systems and conditions these species may reach equilibrium with O^{2-}

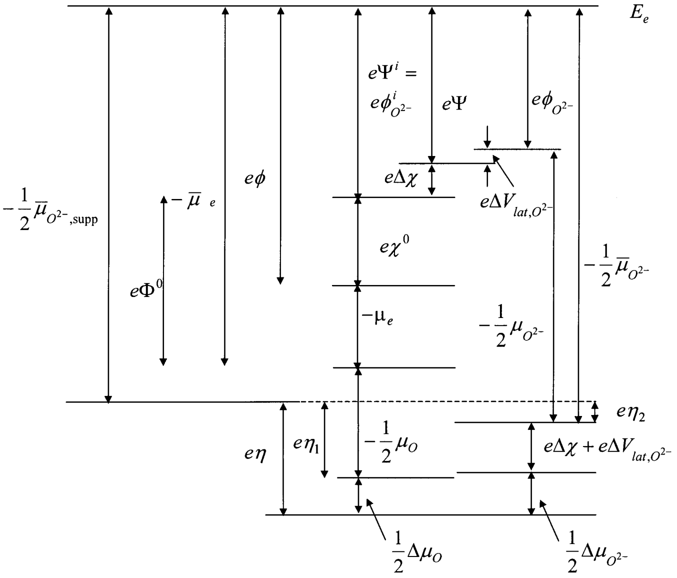

FIG. 7. Energy levels at a metal surface in contact with an oxygen-ion-conducting solid electrolyte while polarised, at steady state. The general case where overpotential may result in a change in adsorbed ionic oxygen chemical potential is shown. Lateral dipole–dipole interactions are neglected under open-circuit conditions; however, their effect under closed-circuit conditions is shown. The reference electrode (not shown) is held at a fixed potential and resistive losses in the electrolyte are considered to be negligible.

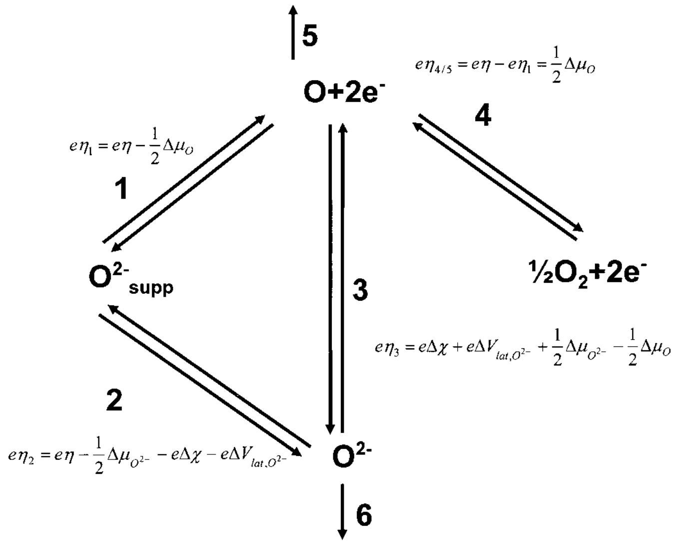

FIG. 8. Reaction network for electrochemical oxygen supply to a metal surface showing driving forces for individual reactions.

in the electrolyte, i.e., the activation overpotential for Reaction 2 goes to zero. There are a number of interesting limiting cases that are worth considering, including slow Reactions 1 and 2, slow Reactions 4 and 5, and slow Reactions 1 and 3 with or without slow Reactions 4 and 5. Here we only consider steady-state behaviour and not the transient behaviour associated with achieving the steady state after polarisation. We also continue to confine ourselves to consideration of a uniform surface, i.e., one with an absence of spatial concentration gradients.

If the kinetics of the charge-transfer reactions (Reactions 1 and 2) are relatively slow then the equilibria on the surface will not be disturbed and the work function cannot be modified. In the case of a reactive system the reaction rate will not be modified although one must allow for the extra supply of oxygen.

If Reactions 4 and 5 are slow then the chemical potential of surface oxygen will be modified and there will be a change in extraction potential. This case has an equivalent effect on the surface as changing the gas-phase composition.

If we introduce the idea that the ionic spillover oxygen is relatively stable, i.e., it is not consumed by reaction with the reducing gas (slow Reaction 6) and it does not easily undergo Reaction 3, then Reaction 2 will be in equilibrium and η_2 will be approximately equal to zero at steady state, i.e., Reactions 1, 3, 4, and 5 are slow. This is an important case as surface ionic oxygen chemical potentials are being dictated by the support while surface oxygen chemical potentials are being dictated by conditions in the gas phase. (It is not the intention of this paper to discuss in detail why such an oxygen-ion spillover species might be stable; however, this could be related to the presence of surface impurities. The presence of sodium, for example, would decrease open-circuit extraction potentials and stabilise oxygen-ion coverages possibly through the formation of some sodium-oxide-like surface species.)

Setting the driving force for Reaction 2 to zero yields the relationships

$$e\eta = e\Delta\chi + e\Delta V_{\text{lat},\text{O}^{2-}} + \frac{1}{2}\Delta\mu_{\text{O}^{2-}}. \qquad [41]$$

The change in surface potential and hence work function depends on any applied overpotential, the change in the energy associated with lateral interactions and the change in the chemical potential of the oxygen ions. In a reactive system the rate of reaction will be modified (26) in addition to the effect of the extra supply of oxygen even though no limiting current is observed if Reactions 4 and 5 are fast compared to Reaction 1.

We may proceed with a very simplistic analysis. If coverages of oxygen ions are neither very low or very high (i.e., intermediate coverages) such that logarithmic terms in the expression for oxygen-ion chemical potential can be neglected relative to other terms in Eq. [41], i.e., Eq. [25] is valid,

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

then

$$e\eta \approx e\Delta\chi + e\Delta V_{\text{lat},\text{O}^{2-}}. \qquad [42]$$

If oxygen-ion coverages are low enough that lateral dipole–dipole interactions can be ignored,

$$e\eta \approx e\Delta\chi, \qquad [43]$$

and we recover the one-to-one relationship between applied overpotential and change in surface potential that has been found experimentally by Vayenas and co-workers (9). However, we note here that this relationship is not generally applicable but is only valid if there is fast surface diffusion of ionic oxygen species, equilibrium between oxygen ions in the electrolyte support and on the catalyst surface, intermediate oxygen-ion coverages and no lateral interaction between surface ions.

Finally we may ask how relevant this result for a solid–electrolyte support is to the general case of mixed ionic-conducting and electronic-conducting supports. Consider the solid–electrolyte electrochemical cell with two metal electrodes, an ideally nonpolarisable electrode exposed to pure oxygen and the other electrode exposed to the same partial pressure of oxygen but also with a reducing gas present. If the cell is now externally short-circuited a flux of oxygen ions will flow. Second, consider a conventional oxide-supported catalyst consisting of the same metal catalyst deposited on a mixed-conducting-oxide support and also exposed to reaction conditions. If the oxide support equilibrates with gas-phase oxygen (but its surface is inert to the reducing gas) and its ionic conductivity is high then the metal catalyst is in the same environment as the metal electrode for the simple reaction network under consideration here. Equations [37] to [40] are obeyed in both cases.

6. CONCLUSIONS

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 ion-conducting support. It is not necessary to suggest that a new form of surface oxygen is formed by charge transfer from the support that would not be otherwise present on the catalyst surface. 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 this basis thermodynamic relationships governing the chemical potentials of the catalyst surface oxygen species are derived for the case of a pure ion-conducting support with fast surface and gas-phase diffusion. It is shown that the catalyst surface potential will change by an amount equal to the applied overpotential for a system satisfying the following conditions: equilibrium between oxygen ions in the electrolyte support and on the catalyst surface, intermediate oxygen-ion coverages, and no lateral interaction between surface ions.

APPENDIX A: THE IONIC OXYGEN CHEMICAL POTENTIAL

Using the Fermi distribution function (e.g., (27)),

$$f = \frac{1}{[1 + \exp(E - E_F)/kT]}, \qquad \text{[A1]}$$

where f is the fractional occupancy of any nondegenerate level at the energy E,

$$f = \frac{\theta_{O^-}}{\theta_O + \theta_{O^-}},$$

and E_F is the Fermi energy, the density of occupied states, i.e., the equilibrium coverage of O^-, will be given by

$$kT \ln \frac{\theta_{O^-}}{\theta_O} = E_F - E_{O/O^-}, \qquad \text{[A2]}$$

with E_{O/O^-} being the energy level associated with the O/O^- transition where

$$E_F = \bar{\mu}_e,$$

and

$$E_{O/O^-} = \bar{\mu}^{\ominus}_{O^-} - \mu^{\ominus}_{O}.$$

We use a single effective energy level and we neglect Franck–Condon effects. Combining with Eq. [19],

$$kT \ln \frac{\theta_{O^-}}{\theta_*} = E_F - E_{O/O^-} + \mu_O - \mu^{\ominus}_{O}. \qquad \text{[A3]}$$

Likewise the coverage of O^{2-} species will be given by

$$kT \ln \frac{\theta_{O^{2-}}}{\theta_{O^-}} = E_F - E_{O^-/O^{2-}}, \qquad \text{[A4]}$$

and therefore

$$kT \ln \frac{\theta_{O^{2-}}}{\theta_*} = 2E_F - E_{O/O^-} - E_{O^-/O^{2-}} - \mu_O - \mu^{\ominus}_{O},$$

with

$$E_{O/O^-} + E_{O^-/O^{2-}} = 2E_{O/O^{2-}} = \bar{\mu}^{\ominus}_{O^{2-}} - \mu^{\ominus}_{O}.$$

Hence

$$kT \ln \frac{\theta_{O^{2-}}}{\theta_*} = 2E_F - 2E_{O/O^{2-}} + \mu_O - \mu^{\ominus}_{O}. \qquad \text{[A5]}$$

As O^- ions are considered to be at a low coverage in comparison with O^{2-} ions (and we can see that an appropriately large value for E_{O/O^-} in Eq. [A3] would result in this) then changing the coverage of doubly charged oxygen ions will also change the value of $E_F - E_{O/O^{2-}}$ as a result of a double-layer effect and hence Eq. [A5] must be revisited. Replacing energy levels with electrochemical potentials in Eq. [A5] gives

$$kT \ln \frac{\theta_{O^{2-}}}{\theta_*} = 2\bar{\mu}_e - \bar{\mu}^{\ominus}_{O^{2-}} + \mu_O. \qquad \text{[A6]}$$

Expressing electrochemical potentials in terms of chemical potentials we get

$$kT \ln \frac{\theta_{O^{2-}}}{\theta_*} = 2\mu_e - 2e\phi - \mu^{\ominus}_{O^{2-}} + 2e\phi_{O^{2-}} + \mu_O,$$

which can also be written as

$$\frac{1}{2}\mu_{O^{2-}} = \frac{1}{2}\mu_O + \mu_e - e\phi + e\phi_{O^{2-}},$$

recovering Eq. [12], with

$$\mu_{O^{2-}} = \mu^{\theta}_{O^{2-}} + kT \ln \frac{\theta_{O^{2-}}}{\theta_*}. \qquad \text{[A7]}$$

APPENDIX B: LATERAL INTERACTIONS

The potential energy associated with one dipole–dipole interaction can be easily shown to be

$$U = \frac{q_{\mathrm{O}^{2-}} q_i}{2\pi\varepsilon_0}\left(\frac{1}{\sqrt{\left(\frac{a_{\mathrm{O}^{2-}} - a_i}{2}\right)^2 + r^2}} - \frac{1}{\sqrt{\left(\frac{a_{\mathrm{O}^{2-}} + a_i}{2}\right)^2 + r^2}}\right), \qquad [\mathrm{B1}]$$

where $q_{\mathrm{O}^{2-}}$ is the charge on the oxygen ion, q_i is the charge on the test ion, $a_{\mathrm{O}^{2-}}$ is the separation distance of the dipole charges for the oxygen ion, a_i is the distance between the test ion and its image, and r is the distance between the dipoles. For $a_{\mathrm{O}^{2-}}$, $a_i \ll r$, this equation reduces to

$$U = \frac{q_{\mathrm{O}^{2-}} q_i a_{\mathrm{O}^{2-}} a_i}{4\pi\varepsilon_0 r^3}. \qquad [\mathrm{B2}]$$

Now we assume that the oxygen dipoles are arranged in a hexagonal array on the catalyst surface around the central test ion or dipole, i.e., the coverage of oxygen ions is much greater than the coverage of any other ion, and therefore the test dipole will have six nearest neighbours and the energy of interaction with them will be

$$U_{\mathrm{r}} = \frac{6 q_{\mathrm{O}^{2-}} q_i a_{\mathrm{O}^{2-}} a_i}{4\pi\varepsilon_0 r^3}. \qquad [\mathrm{B3}]$$

If we approximate the hexagonal array of oxygen dipoles as a series of concentric circles whereby the distance form the central test dipole to the n^{th} circle is nr with the number of dipoles associated with that circle being $6n$, then the total energy associated with the presence of the test dipole due to lateral coulombic interactions will be

$$U_{\mathrm{lat},i} = \sum_{1}^{\infty} \frac{6 q_{\mathrm{O}^{2-}} q_i a_{\mathrm{O}^{2-}} a_i}{4\pi\varepsilon_0 n^2 r^3}. \qquad [\mathrm{B4}]$$

However,

$$\sum_{1}^{\infty} \frac{6}{n^2} = \pi^2,$$

and therefore

$$U_{\mathrm{lat},i} = \frac{\pi q_{\mathrm{O}^{2-}} q_i a_{\mathrm{O}^{2-}} a_i}{4\varepsilon_0 r^3}. \qquad [\mathrm{B5}]$$

This can be expressed in terms of coverages or surface density of dipoles by using

$$\theta_{\mathrm{O}^{2-}} = \frac{4 r_{\mathrm{O}^{2-}}^2}{r^2} = \frac{n_{\mathrm{O}^{2-}}}{N},$$

where $r_{\mathrm{O}^{2-}}$ is the effective ionic radius of the oxygen ion, giving

$$U_{\mathrm{lat},i} = \frac{\pi q_{\mathrm{O}^{2-}} q_i a_{\mathrm{O}^{2-}} a_i}{32\varepsilon_0 r_{\mathrm{O}^{2-}}^3}\theta_{\mathrm{O}^{2-}}^{3/2}. \qquad [\mathrm{B6}]$$

Knowing the area occupied by an oxygen ion in a hexagonal array,

$$N = \frac{1}{2\sqrt{3} r_{\mathrm{O}^{2-}}^2},$$

and using the definition of dipole moment of the oxygen ion,

$$\mu = q_{\mathrm{O}^{2-}} a_{\mathrm{O}^{2-}}. \qquad [\mathrm{B7}]$$

Equation [B6] becomes

$$U_{\mathrm{lat},i} = \frac{N q_i \mu}{\varepsilon_0}\frac{\pi\sqrt{3}}{16}\frac{a_i}{r_{\mathrm{O}^{2-}}}\theta_{\mathrm{O}^{2-}}^{3/2}, \qquad [\mathrm{B8}]$$

and therefore

$$V_{\mathrm{lat},i} = \frac{U_{\mathrm{lat},i}}{q_i} = \frac{N\mu}{\varepsilon_0}\frac{\pi\sqrt{3}}{16}\frac{a_i}{r_{\mathrm{O}^{2-}}}\theta_{\mathrm{O}^{2-}}^{3/2}. \qquad [\mathrm{B9}]$$

If the central ion is replaced by an oxygen ion we see that

$$U_{\mathrm{lat},\mathrm{O}^{2-}} = \frac{N q_{\mathrm{O}^{2-}} \mu}{\varepsilon_0}\frac{\pi\sqrt{3}}{16}\frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}}\theta_{\mathrm{O}^{2-}}^{3/2} \qquad [\mathrm{B10}]$$

$$V_{\mathrm{lat},\mathrm{O}^{2-}} = \frac{U_{\mathrm{lat},\mathrm{O}^{2-}}}{q_{\mathrm{O}^{2-}}} = \frac{N\mu}{\varepsilon_0}\frac{\pi\sqrt{3}}{16}\frac{a_{\mathrm{O}^{2-}}}{r_{\mathrm{O}^{2-}}}\theta_{\mathrm{O}^{2-}}^{3/2}. \qquad [\mathrm{B11}]$$

NOMENCLATURE

Letters

a_i	Separation of dipole charges for the ith species
e	Charge on an electron
E	Energy
E_{e}	Energy on a free electron at infinity
E_{F}	Fermi energy
$E_{\mathrm{O/O^-}}$	Energy associated with the O/O$^-$ transistion
f	Fractional occupancy of an electronic state
G	Gibb's free energy
k	Boltzmann constant
n	Refers to the nth circle of dipoles surrounding a central dipole
n_i	Density of surface sites occupied by the ith species
N	Density of surface sites
q_i	Charge associated with the ith species
r	Distance between dipoles
$r_{\mathrm{O}^{2-}}$	Effective ionic radius of a surface oxygen ion
R	Reaction rate
U	Potential energy associated with one dipole–dipole interaction
U_{lat}	Potential energy associated with one dipole interacting with all other surface dipoles

U_r	Potential energy associated with one dipole interacting with its nearest neighbours
$V_{\mathrm{lat},i}$	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. [2]
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
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
ξ	Constant used in Eq. [3]
Ψ	Outer potential

Superscripts

$\ominus$	Standard state
0	Unpolarised condition
i	Immediately after polarisation but before appreciable spillover has occurred

Subscripts

sd	Surface diffusion
supp	Associated with the catalyst support

REFERENCES

1. Delmon, B., and Froment, G. F., *Catal. Rev.-Sci. Eng.* **38**, 69–100 (1996).
2. Vayenas, C. G., Bebelis, S., Yentekakis, I. V., and Lintz, H.-G., *Catal. Today* **11**, 303–442 (1992).
3. Vayenas, C. G., Jaksic, M. M., Bebelis, S., and Neophytides, S. G., *in*“Modern Aspects of Electrochemistry” (P. Horsman, B. E. Conway, and R. E. White, Eds.), Vol. 29, p. 57. Plenum Press, New York, 1996.
4. Vayenas, C. G., and Neophytides, S. G., “Catalysis,” Vol. 12, Chap. 6, Royal Chem. Soc., Cambridge, 1996.
5. Bebelis, S., Makri, M., Buekenhoudt, A., Luyten, J., Brosda, S., Petrolekas, P., Pliangos, C., and Vayenas, C. G., *Solid State Ionics* **129**, 33–46 (2000).
6. Yentekakis, I. V., and Vayenas, C. G., *J. Catal.* **111**, 170–188 (1998).
7. Vayenas, C. G., Bebelis, S., Neophytides, S., and Yentekakis, I. V., *Appl. Phys. A* **49**, 95–103 (1989).
8. Bebelis, S., and Vayenas, C. G., *J. Catal.* **118**, 125–146 (1989).
9. Vayenas, C. G., Bebelis, S., and Ladas, S., *Nature (London)* **343**, 625 (1990).
10. Vayenas, C. G., and Neophytides, S., *J. Catal.* **127**, 645–664 (1991).
11. Neophytides, S., and Vayenas, C. G., *J. Catal.* **118**, 147–163 (1989).
12. Vayenas, C. G., Bebelis, S., and Despotopoulou, M., *J. Catal.* **128**, 415–435 (1991).
13. Politova, T. I., Sobyanin, V. A., and Belyaev, V. D., *React. Kinet. Catal. Lett.* **41**, 321 (1990).
14. Makri, M., Buekenhoudt, A., Luyten, J., and Vayenas, C. G., *Ionics* **2**, 282 (1996).
15. Tsiplakides, D., Neophytides, S., Enea, O., Jaksic, M. M., and Vayenas, C. G., *J. Electrochem. Soc.* **144**, 2072 (1997).
16. Yentekakis, I. V., and Vayenas, C. G., *J. Catal.* **149**, 238 (1994).
17. Pliangos, C., Yentekakis, I. V., Ladas, S., and Vayenas, C. G., *J. Catal.* **159**, 189 (1996).
18. Emery, D. A., Middleton, P. H., and Metcalfe, I. S., *Surf. Sci.* **405**, 308–315 (1999).
19. Emery, D. A., Lucke, R. J. C., Middleton, P. H., and Metcalfe, I. S., *J. Electrochem. Soc.* **146**, 2188–2193 (1999).
20. Emery, D. A., Middleton, P.H., and Metcalfe, I. S., *J. Electrochem. Soc.* **146**, 2194–2198 (1999).
21. Vayenas, C. G., and Tsiplakides, D., *Surf. Sci.* **467**, 23–34 (2000).
22. Poppe, J., Völkenming, S., Schaak, A., Schütz, E., Janek, J., and Lmbihl, R., *Phys. Chem. Chem. Phys.* **1**, 5242 (1999).
23. Poppe, J., Schaak, A., Janek, J., and Imbihl, R., *Ber. Bunsenges. Phys. Chem.* **102**, 1019–1022 (1998).
24. Luerßen, B., Gunther, S., Marbach, H., Kiskinova, M., Janek, J., and Imbihl, R., *Chem. Phys. Lett.* **316**, 331–335 (2000).
25. Janek, J., Rohnke, M., Luerßen, B., and Imbihl, R., *Phys. Chem. Chem. Phys.* **2**, 1935–1941 (2000).
26. Metcalfe, I. S., *J. Catal.* **199**, 259–272 (2001).
27. Morrision, S. R., “The Chemical Physics of Surfaces,” 2nd Edition. Plenum Press, New York, 1990.