A first-principles study of molecular oxygen dissociation at an electrode surface: a comparison of potential variation and coadsorption effects

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Supplementary Information

Determination of Surface Workfunction

The methods used to determine the system workfunction, which is subsequently related to the electrode potential on both absolute and normal hydrogen electrode scales as discussed in the text, are described below.

Vacuum slab. The vacuum slab model is illustrated in Figure S1a for Na and O_2 coadsorbed. The mirrored slab construction also allows for definitive determination of the electrostatic potential at the center of the vacuum layer, and therefore avoids asymmetry in assignment of the slab workfunction. Figure S1b plots the average electrostatic potential in the plane parallel to the surface ("*xy*" plane) as a function of the surface-perpendicular ("*z*") position in the cell. Slab workfunctions were calculated by referencing the system Fermi level to the average Coulombic potential in the xy plane at the center of the vacuum layer. The energy (*x*) axis of the density of states and local density of states plots are also referenced to this potential.

Solvated slab. The determination of the surface workfunction in the solvated system is complicated by the absence of a distinct vacuum layer and by the asymmetry of the slab. Figure S1d illustrates the averaged Coulombic potential (across the *xy*-plane) as a function of *z*-position (perpendicular to the surface) in the solvated cell. A method described by Taylor *et al.*[6] was used to reference the metal Fermi level to the vacuum potential. In this method, a 20 Å vacuum layer is introduced in the middle of the water layer, as illustrated in Figure S1e. A single-point calculation is then used to determine the *xy*-averaged Coulombic potential in this vacuum reference system, as illustrated in Figure S1f. The potential at the center of the vacuum region, ϕ_{vac}, is defined as the vacuum potential, and all other Coulombic potentials of the vacuum reference system are referenced versus this vacuum potential (as potential versus vacuum). In the closed system, the absolute value of the Coulombic potential at the center of the metal slab, ϕ_M, is set to equal the corresponding metal slab potential (referenced versus vacuum) for the open system. The potential shift necessary to equate these two values is also applied to the metal Fermi level, therefore referencing the Fermi level versus vacuum and providing a measure of the solvated surface workfunction. The assignment of the vacuum potential for the open system is inherently approximate due to the asymmetry of the two sides of the solvated slab, which leads to a net dipole across the solvated slab, and therefore a sloped potential across the vacuum region. Taylor *et al*. illustrated that this approximation is equivalent to the approximation that the capacitance associated with each of the two slab sides is the same.[6] This approximation was found to introduce only an insignificant error in workfunction determination, as both sides of the

slab represent an adsorbed water layer and only small changes in workfunction occur when a surface water molecule is replaced with O_2 or Na. This approximation has been made in numerous studies using the double-reference method to probe adsorption at solvated interfaces.[5,6,30,32] Consistent and reliable comparison of calculated data with experimental systems suggests that the error introduced in this assignment is considerably less than ± 0.25 eV.

**Variation of the electrode potential with varying system charge**

Using the double-reference method of Filhol and Neurock,[5,6] the metal Fermi level is referenced versus the vacuum potential as the charge on the model system is varied. The first reference of this system is as described above, used to reference the Fermi level in the $q0$ system versus vacuum. The second reference refers to the determination of the Fermi level in the various $q{\neq}0$ charged systems versus the vacuum potential. To do this, the potential at the center of the water layer is taken to remain constant as the system charge is varied, and therefore equal to that for the $q0$ system, as shown by Taylor et al.[6] This reference point within the water layer (water vs. vacuum) enables the Fermi level of each charged system to be referenced versus vacuum. This method is extensively described by Taylor et al.,[6] and the reader is referred to this source for comparison of the interfacial electric field with that created by inclusion of explicit electrolyte ions in the model system.

Double-reference quadratic fit constants for total energy versus potential

Using the double-reference method, the total energy of each system was determined at 5 different system charges (q= -1, -0.5, 0, 0.5, 1 per unit cell), and these five data points were fit to a quadratic relationship via Eq. 3 to give a continuous energy versus potential relationship. Table S1 provides the quadratic fit constants determined for each system.

Table S1. Constants for quadratic fit of the indicated system energy versus potential using Eq. 3.

Systems	A	B	C
$24H_2O$	-0.599	0.170	-508.079
$Na + 23H_2O$	-0.587	0.299	-494.941
$O_2 + 23H_2O$	-0.459	0.372	-504.276
$2O + 23 H_2O$	-0.477	0.313	-504.929
Dissoc. TS + $23H_2O$	-0.489	0.360	-503.780
$O_2 + Na + 22H_2O$	-0.484	0.460	-493.114
$2O + Na + 22H_2O$	-0.534	0.427	-493.767
Dissoc. TS + $22H_2O$	-0.565	0.429	-492.680
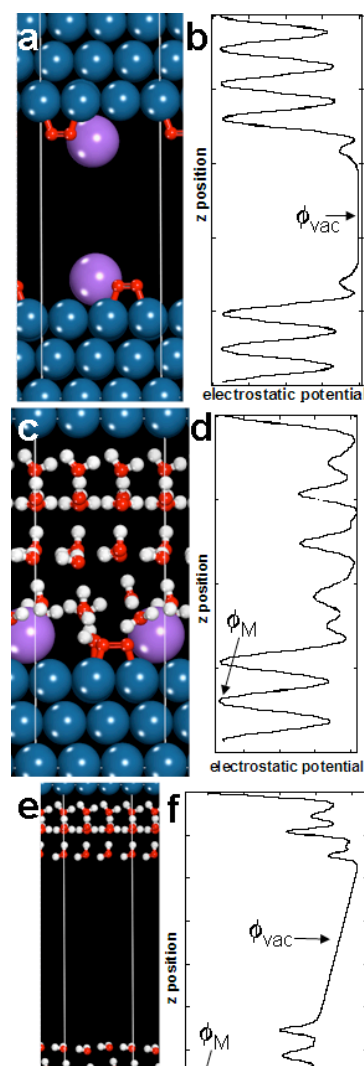
Figure S1. Example structures for the optimized vacuum slab (a) and fully solvated (c) systems and for the reference cell to determine the reference potential (e), where a vacuum layer region is inserted into the solvated model. Corresponding electrostatic potential averaged across the xy-plane is plotted versus the surface normal position in the cell are given in plots b, c and d for structures a, c, and e, respectively. Specific potential values used to reference to the vacuum potential (ϕ_{vac} and ϕ_M) are labeled.