Supporting Information

A Multiscale Modelling Approach to Elucidate the Mechanism of the Oxygen Evolution Reaction at the Hematite-Water Interface
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Force profile from constrained DFT-MD

![Force profile](image)

*Figure-SI-1. Force profile obtained from DFT-MD simulations. Each point was run for 3-5 ps and the resulting profile was integrated to construct the Gibbs free energy profile reported in the main text (Figure 5).*

Force and Gibbs free energy profiles from steered MD using slow growth approach

![Force and Gibbs profiles](image)

*Figure-SI-2. (left) force profile from slow growth approach simulations to simulate the proton transfer reaction. (right) Gibbs free energy profile for the proton transfer reaction obtained by integrating the force profile.*
Comparison of OH coverage for mechanisms M1 and M2

Figure-SI- 3. Comparison of surface coverage of OH (y-axis) as a function of time (x-axis) for various values of the applied bias for mechanisms M1 (red, with H$_2$O adsorption) and M2 (black, without H$_2$O adsorption).

Comparison of O$_2$ evolution for mechanisms M1 and M2

Figure-SI- 4. Comparison of O$_2$ evolution as a function of time for various values of the applied bias for mechanisms M1 (red, with H$_2$O adsorption) and M2 (black, without H$_2$O adsorption).

Rate constants for kMC

Rate of individual steps in kMC were determined by eq(13) as described in the main text.
The adsorption of water was modelled as follows:

Forward reaction, adsorption: \( A_f = 10^5 \ \text{s}^{-1} \) and \( G_f = 0.00 \ \text{eV} \)

Backward reaction, desorption: \( A_b = 1 \) and \( G_b = 0.2 \ \text{eV} \)

For modelling the adsorption/desorption of water the parameters \( \{A_f, A_b, G_f, G_b\} \) were chosen to ensure that most of the wall-time is kMC simulations is not used in simulating fast reversible process of adsorption of water. For rest of the steps which are all electrochemical in nature we used the same pre-factors \( (A_f = A_b = 10^{14} \ \text{s}^{-1}) \) for the forward and the backward reaction.

\[ k_f^i = A_f \ast \exp \left( -\frac{G_f^i}{k_B T} \right) \] (13a)

\[ k_b^i = A_b \ast \exp \left( -\frac{G_b^i}{k_B T} \right) \] (13b)

Table-SI-1. TS barriers for forward and backward reactions in mechanism M1 for selected values of V. Potential dependent rate constants can be evaluated from this data using eq(13)

<table>
<thead>
<tr>
<th>V</th>
<th>TS(( \text{H}_2\text{O} \rightarrow \text{OH} ))</th>
<th>TS(( \text{OH} \rightarrow \text{H}_2\text{O} ))</th>
<th>TS(( \text{O} \rightarrow \text{OH} ))</th>
<th>TS(( \text{OH} \rightarrow \text{O} ))</th>
<th>TS(( \text{O}_2 \rightarrow \text{OH} ))</th>
<th>TS(( \text{OH} \rightarrow \text{O}_2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.82</td>
<td>0.11</td>
<td>2.29</td>
<td>0.11</td>
<td>1.30</td>
<td>0.11</td>
</tr>
<tr>
<td>0.8</td>
<td>1.02</td>
<td>0.11</td>
<td>1.49</td>
<td>0.11</td>
<td>0.5</td>
<td>0.11</td>
</tr>
<tr>
<td>1.0</td>
<td>0.82</td>
<td>0.11</td>
<td>1.29</td>
<td>0.11</td>
<td>0.30</td>
<td>0.11</td>
</tr>
<tr>
<td>1.23</td>
<td>0.59</td>
<td>0.11</td>
<td>1.06</td>
<td>0.11</td>
<td>0.07</td>
<td>0.11</td>
</tr>
<tr>
<td>1.30</td>
<td>0.52</td>
<td>0.11</td>
<td>0.99</td>
<td>0.11</td>
<td>0.00</td>
<td>0.11</td>
</tr>
<tr>
<td>1.50</td>
<td>0.32</td>
<td>0.11</td>
<td>0.79</td>
<td>0.11</td>
<td>0.00</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Representative INCAR files

Geometry Optimizations

SYSTEM = Fe2O3 ionic relaxation
ICHARG = 1 initial charge density option
ISTART = 1 initial wavefunctions option
PREC = Medium precision of calculation
NELM = 60 max number of electronic steps
NELMIN = 2 min number of electronic steps
EDIFF = 1E-04 energy stopping criterion for electronic iterations
EDIFFG = -1E-02 force stopping criterion for geometric
LREAL = A real-space projection
ALGO = Very Fast choose algorithm
NSIM = 4 parallelization option
ISPIN = 2 spin-polarization option
ISYM = 0 turns symmetry calculation on or off
ISIF = 2 geometrical relaxation mode
NSW = 300 max number of geometry steps
IBRION = -2 ionic relaxation method
POTIM = .07 time step for geometrical optimization
ISMEAR = 0 smearing method
SIGMA = .100 broadening in eV
ENCUT = 700
MAGMOM = 72*0 24*-4 24*4  # corresponding to 72 O and 48 Fe
RWIGS = 0.8 1.2
LDAU = .TRUE.
LDAUTYPE = 2
LDAUL = -1 2
LDAUU = 0.0 4.30
LDAUJ = 0.0 0.00
LDAUPRINT = 2
LWAVE = F
LSOL = T

DFT-MD simulations

SYSTEM   = Fe2O3
# Start parameter for this run:
!   NWRITE =      2
!   PREC =     low
ISTART =      1
ICHARG =      1
ISPIN  =      2
!   NBANDS =     120
!   MAGMOM =      32*-4.0  32*4.0   96*0.0   208*0.0
!   LNONCOLLINEAR =  F
!   LSORBIT=      F
!   INIWAV =      1
!   LASPH =      F
!   METAGGA=      F
# Electronic Relaxation 1
ENCUT   =  500.0 eV
ENAUG   =  600.0 eV
EDIFF   =  1E-06
LREAL   =  Auto
!   VOSKOWN =  1
!   NELM    = 40
NELM    = 40;   NELMIN=  8
!   ENINI   =  200.0
!   LCOMPAT =  F
!   LREAL_COMPAT= F
!   GGA_COMPAT  = T
!   LMAXPAW     = -100
!   LMAXMIX     =    2
!   ROPT        =    0.00000
# Electronic relaxation 2 (details)
ALGO   =   Very Fast
!   IALGO  =     38
!   LDIAG  =      T
!   IMIX   =   4
!   AMIX   =  0.80;   BMIX   =  1.00
!   AMIX_MAG =  3.20;   BMIX_MAG =  1.00
!   AMIN   =  0.10
!   WC     =  100.;   INIMIX=   1;  MIXPRE=  1
# Ionic relaxation
The CONTCAR files from geometry optimizations with and without VASPsol, and the force profiles from constrained DFT-MD simulations are provided separately as a .zip file.
Molecular models of hematite in DFT and DFT-MD simulations

Figure-SI- 5. (top) Different views of the pristine hematite 110 surface (48 Fe, 72 O; hexagonal representation) used in DFT calculations. (bottom) an extended view with using periodic boundary conditions.

Figure-SI- 6. (top) Different views of the pristine hematite 110 surface (64 Fe, 96 O; rhombohedral representation) used in DFT-MD calculations. (bottom) an extended view with using periodic boundary conditions.