Supporting Information

A Multiscale Modelling Approach to Elucidate the Mechanism of the Oxygen Evolution Reaction at the Hematite-Water Interface

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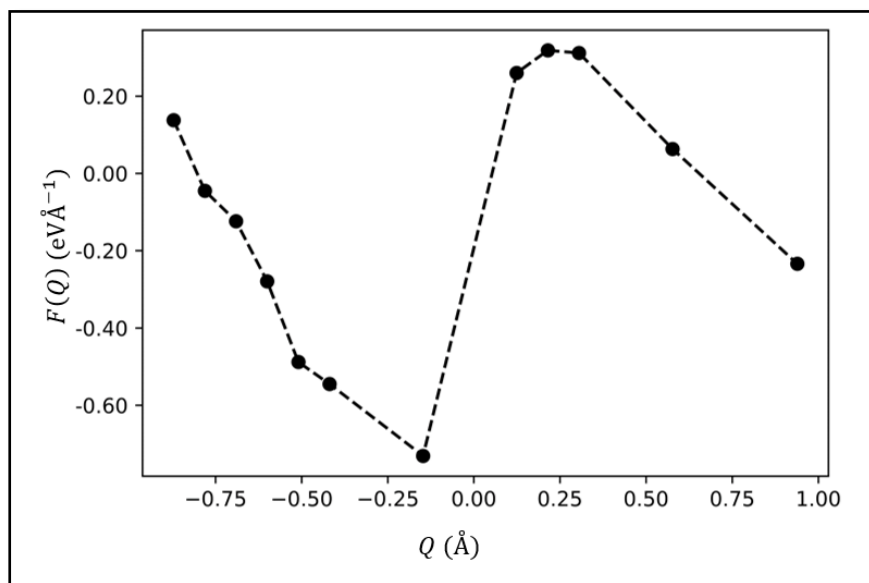
Force profile from constrained DFT-MD

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).

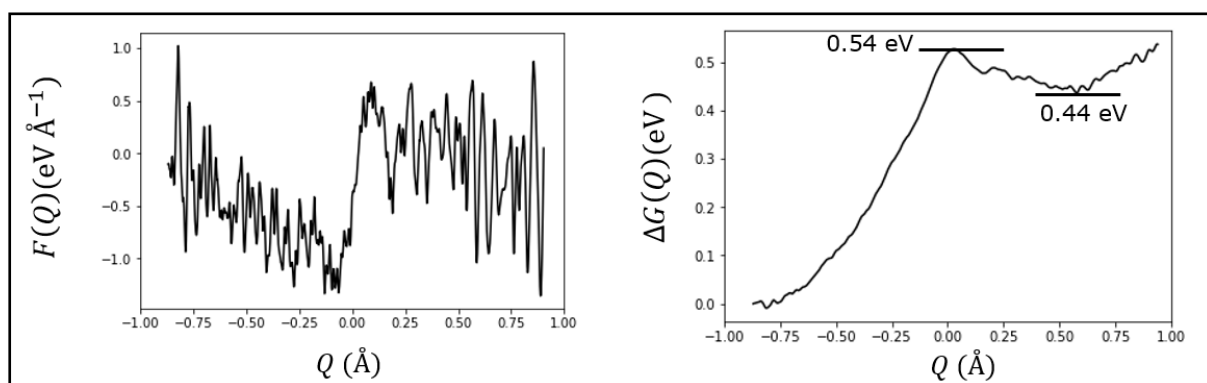# Force and Gibbs free energy profiles from steered MD using slow growth approach

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.

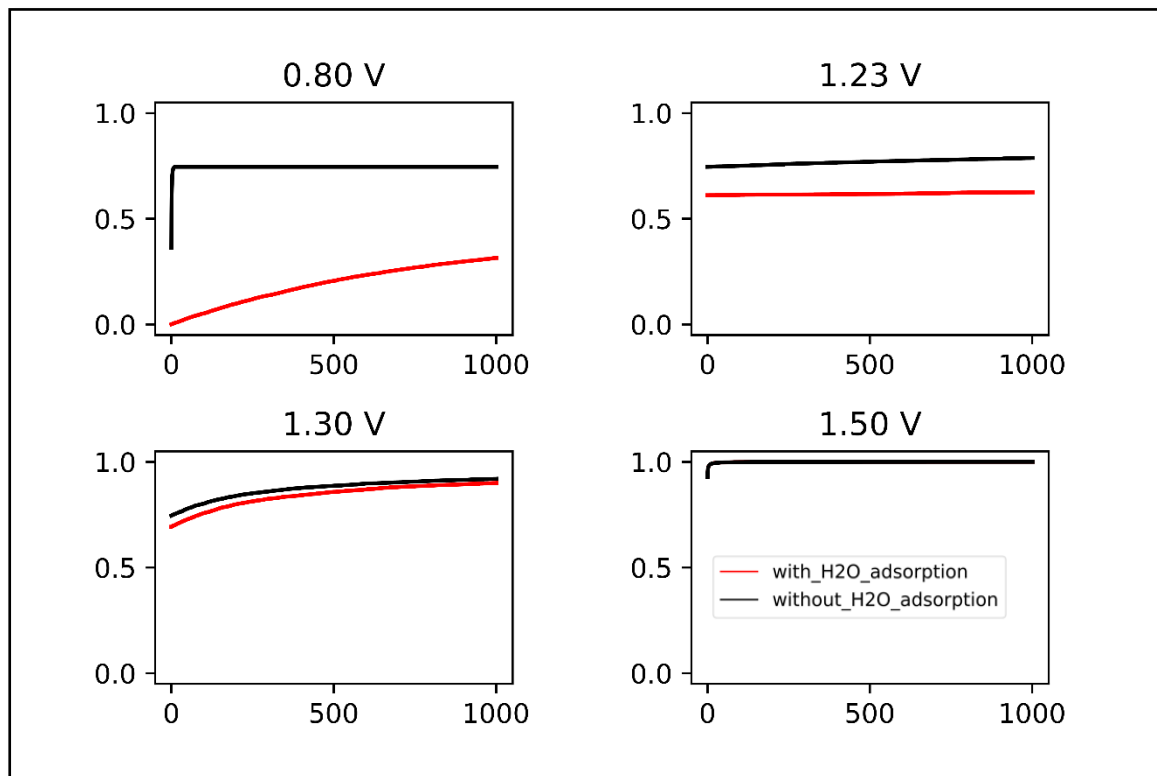## Comparison of OH coverage for mechanisms M1 and M2

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_2O adsorption) and M2 (black, without H_2O adsorption).

Comparison of O_2 evolution for mechanisms M1 and M2
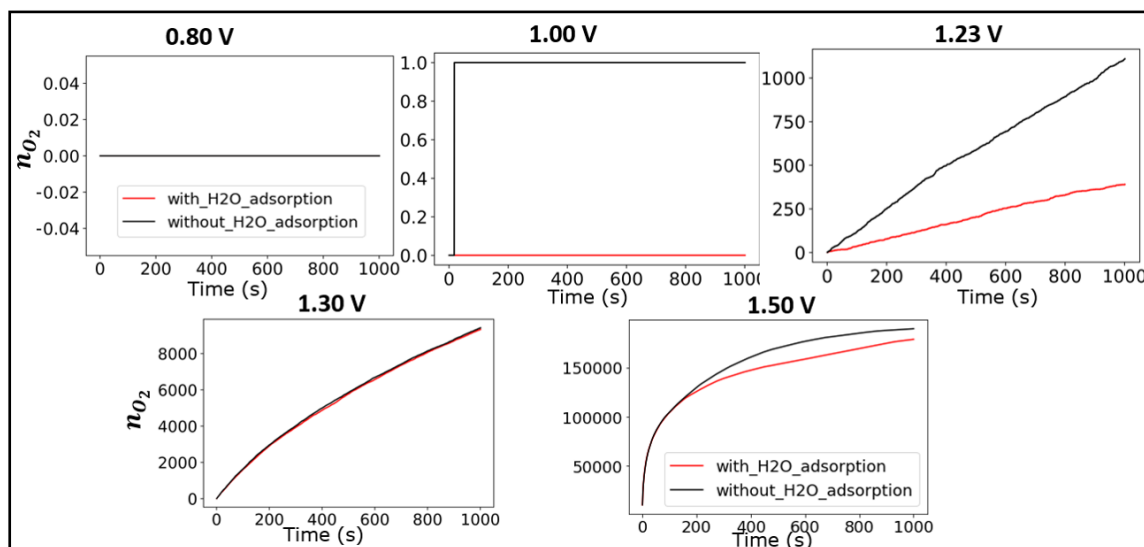

Figure-SI- 4. Comparison of O_2 evolution as a function of time for various values of the applied bias for mechanisms M1 (red, with H2O adsorption) and M2 (black, without H2O adsorption).

Rate constants for kMC

Rate of individual steps in kMC were determined by eq(13) as described in the main text

$$k_f^i = A_f * \exp\left(-\frac{G_f^i}{k_B T}\right) \qquad (13a)$$

$$k_b^i = A_b * \exp\left(-\frac{G_b^i}{k_B T}\right) \qquad (13b)$$

The adsorption of water was modelled as follows:

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

Backward reaction, desoprtion: $A_b = 1$ and $G_b = 0.2$ eV

For modelling the adsorption/desoprtion 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 ($A_f = A_b = 10^{14} \ s^{-1}$) for the forward and the backward reaction.

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)

V	$TS_{\{H_2O \rightarrow OH\}}$	$TS_{\{OH \rightarrow H_2O\}}$	$TS_{\{OH \rightarrow O\}}$	$TS_{\{O \rightarrow OH\}}$	$TS_{\{O \rightarrow OOH\}}$	$TS_{\{OOH \rightarrow O\}}$	$TS_{\{O_2 \rightarrow OOH\}}$	$TS_{\{OOH \rightarrow O_2\}}$
0.0	1.82	0.11	2.29	0.11	1.30	0.11	0.11	0.11
0.8	1.02	0.11	1.49	0.11	0.5	0.11	0.00	0.11
1.0	0.82	0.11	1.29	0.11	0.30	0.11	0.00	0.11
1.23	0.59	0.11	1.06	0.11	0.07	0.11	0.00	0.11
1.30	0.52	0.11	0.99	0.11	0.00	0.11	0.00	0.11
1.50	0.32	0.11	0.79	0.11	0.00	0.11	0.00	0.11

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 = 0.00 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
```

```
!   EDIFFG  =
!   ISIF    =
    NSW     =   1000
    IBRION  =     0
!   NBLOCK  =    1;  KBLOCK =     1
!   NFREE   =     0
!   IWAVPR  =    10
    ISYM    =     0
!   LCORR   =     T
    POTIM   =  0.50
!   TEIN    = 350
    TEBEG   = 350.0;   TEEND = 350.0
    SMASS   = 0
!   NPACO   =    256;   APACO = 16.0
!   PSTRESS =   0.0
!   MDALGO  =    11

# DOS related values:
    ISMEAR =    0;   SIGMA  =  0.05
!   EMIN  = 10.00;   EMAX  =-10.00
# Write flags
    LWAVE   =     F
    LCHARG  =     F
    LVTOT   =     F
!   LELF    =
!   LORBIT  =
#  Atomic Wigner-Seitz radii
!   RWIGS   = -1.00
!   NELECT  =     1.0000
!   NUPDOWN =    -1.0000
#  Mass of Ions in am
   #Fe  Fe  O   O      O   H
    POMASS  =   55.8 55.8 16.0 16.0 16.0 2.0  # Deuterium mass for H
# BLYP
    GGA   = B5
    ALDAX = 1.00
    AGGAX = 1.00
    AGGAC = 1.00
    ALDAC = 0.00
# vdW correction
    IVDW   = 12
    LVDWSCS = .TRUE.
# meta dynamics
    MDALGO    = 2
!   HILLS_H   = 0.1E-2
!   HILLS_W   =
!   HILLS_BIN = 50
    LBLUEOUT   = .TRUE.
!    INCREM   = 0.0005
NPAR = 16
```

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.

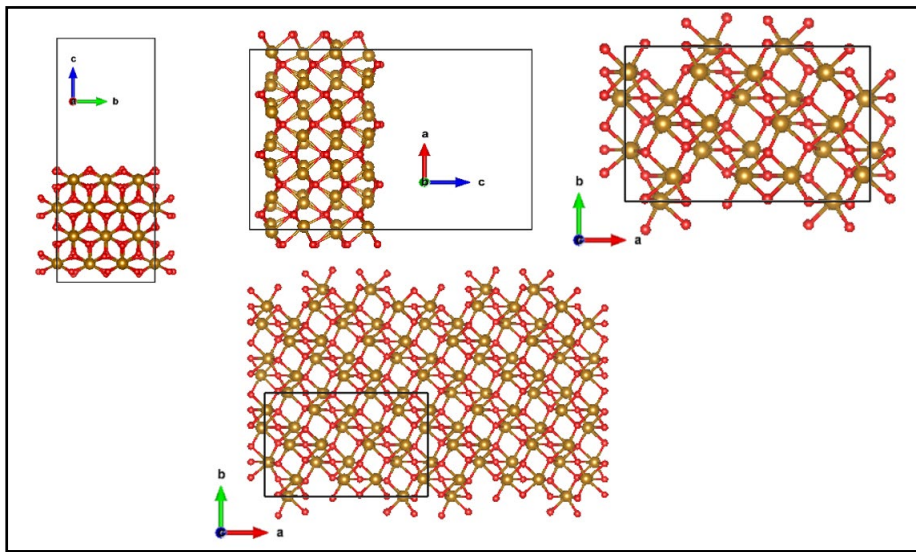# Molecular models of hematite in DFT and DFT-MD simulations

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.
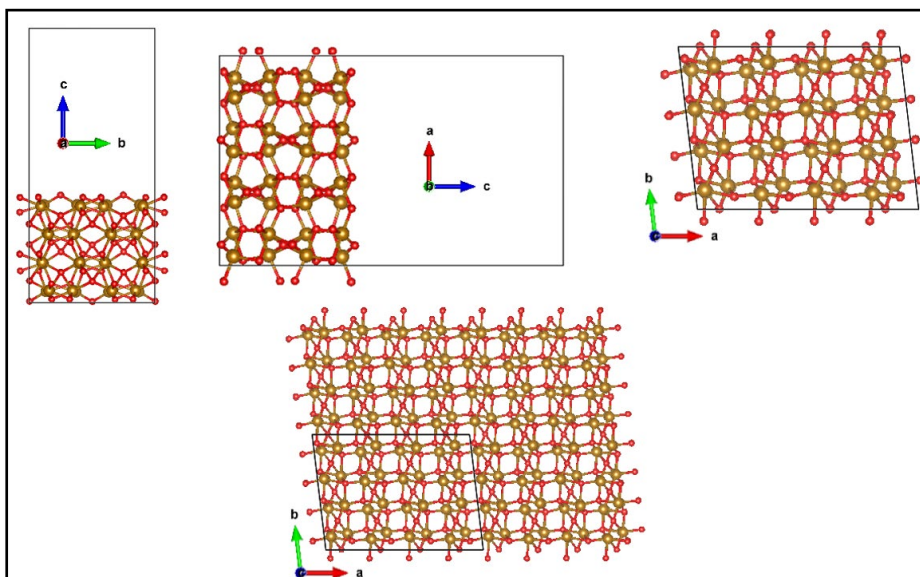

Figure-SI- 6. (top) Different views of the pristine hematite 110 surface (64 Fe, 96 O; rhomobohedral representation) used in DFT-MD calculations. (bottom) an extended view with using periodic boundary conditions.