

Supporting Information:

**Identifying water oxidation
evolution reaction bottleneck by *Ab-
initio* analysis of in-situ optical
absorbance spectrum**

*Natav Yatom, Yuval Elbaz, Shelly Navon, and Maytal Caspary Toroker**

Department of Materials Science and Engineering, Technion - Israel Institute of Technology,
Haifa 3200003, Israel

This supporting information includes:

1. INCAR, VASP commend file for frequency-dependent, dielectric-matrix (3x3) calculation within the Random Phase Approximation (RPA).
2. Iron oxidation state analysis.

*Corresponding author: maytalc@technion.ac.il

1. INCAR file

INCAR commend file for the dielectric matrix calculation of the *OH intermediate slab.

```
ISTART = 1
PREC = Accurate
ALGO = Very_Fast
EDIFF = 1E-4
NELM = 1000
MAGMOM = 13*0 4*4 4*-4 6*0
LVTOT = .TRUE.
LAECHG = .TRUE.
ISMear = -5
SIGMA = 0
EMIN = -8.5
EMAX = 20
NEDOS = 20000
LOPTICS = .TRUE.
LWAVE = .TRUE.
LCHARG = .TRUE.
ISPIN = 2
ISYM = 0
EDIFFG = -3.0E-2
LORBIT = IBRION = 2          NSW = 50
ISIF = 0
POTIM = 0.3
LREAL = .FALSE.
NSIM = 1
NPAR = 24
KPAR=4
NBANDS = 360
ENCUT = 700 eV
LDAU = .TRUE.
LDAUTYPE = 2
LDAUL = -1 2 -1
LDAUU = 0 4.3 0
LDAUJ = 0 0 0
LDAUPRINT = 0
```

2. Iron oxidation state analysis

The oxidation state analysis is based on magnetic moment, Bader charge, and DOS calculations. We compare the result of surface iron atoms with those in the bulk for the five intermediates.

Table 1S- Calculated Bader charge in units of e (electron charge) and calculated magnetic moment in units of μ_B (Bohr magneton) for the iron atom next to the active site ("*") and the oxygen atom above the active site ("*").

Unit cell	Oxygen atom above *	Iron atom next to *		
	Bader charge [e]	Bader charge [e]	Magnetic moment [μ_B]	Interpreted oxidation state
Bulk	-1.2	+1.8	4.2	+3
*	-1.2	+1.4	3.7	+2
*OH ₂	-1.2	+1.4	3.7	+2
*OH	-1.2	+1.8	4.2	+3
*O	-0.9	+1.8	3.7	+4
*OOH	-0.6	+1.8	4.2	+3

Oxidized iron, as a first row transition metal gives away two 4s electrons before the 3d electrons. As result, Fe(+3) in Fe₂O₃ has a $5\mu_B$ magnetic moment, as illustrated in Figure 1S. In this state any additional oxidation or reduction can only reduce its magnetic moment. Iron's calculated magnetic moment in the bulk is $4.2\mu_B$ and not $5\mu_B$, as result of electronic density smearing to the neighboring oxygen atoms. Thus we can correlate each of the five uncoupled 3d electrons to $4.2/5=0.84\mu_B$.

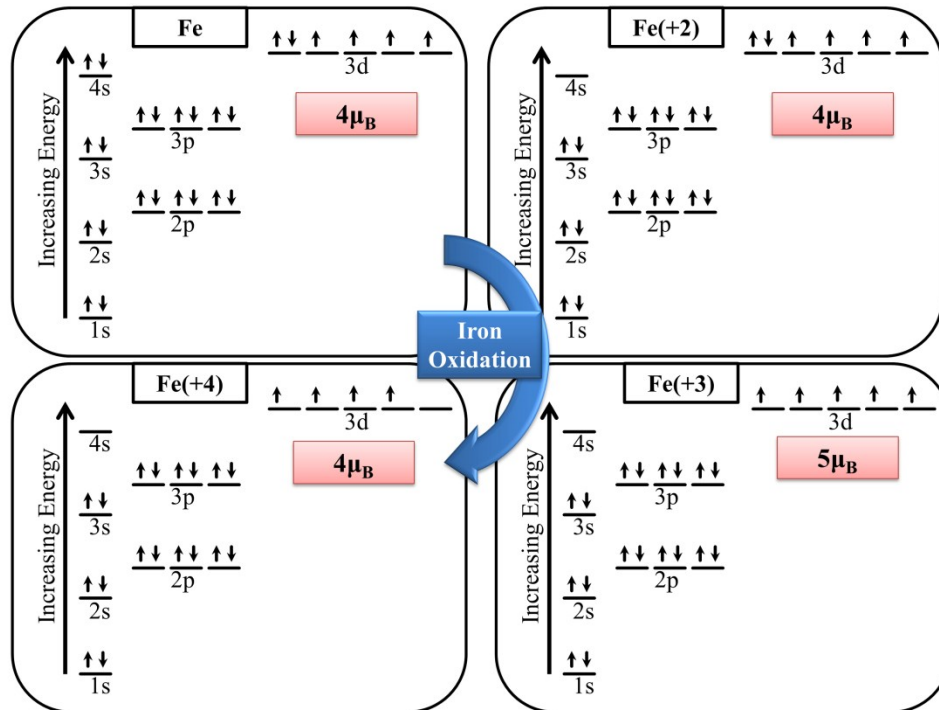


Figure 1S- Iron electronic configuration. Iron in its +2, +3, and +4 oxidation states has a magnetic moment of $4\mu_B$, $5\mu_B$, and $4\mu_B$, respectively.

*OH₂ intermediates:

Iron Bader charge is -0.4 relative to the bulk and Fe_d mid-gap states are occupied (Figure 5.a,b), indicating an additional 3d electron to the bulk iron +3 configuration. Iron magnetic moment is 3.7μ_B correspond to four uncoupled 3d electrons 0.84*4=3.36μ_B. All implying iron is in its +2 oxidation state.

*OH intermediate:

Bader charge, density of states (DOS) (Figure 5.c.), and magnetic moment is similar to the bulk, indicating iron is in the +3 oxidation state.

*O intermediate:

While iron Bader charge is similar to the bulk, the oxygen Bader charge is 0.3 different relative to the bulk. Fe_d mid-gap states are unoccupied and hybridized with O_p states (Figure 5.d.). Both Bader charge and DOS indicate a missing electron on FeO relative to the bulk electronic configuration. Iron magnetic moment is 3.7μ_B correspond to four uncoupled 3d electrons 0.84*4=3.36μ_B. Therefore, there is a hole on surface oxygen and iron is in its +4 oxidation state. Occupying the hole state will induce the creation of an Fe(+4)=O bond.

*OOH intermediate:

While iron Bader charge is similar to the bulk, the oxygens Bader charge is 0.6 different relative to the bulk. Fe_d mid-gap states are unoccupied deep in the conduction band (Figure 5). Iron magnetic moment is 4.2μ_B correspond to five uncoupled 3d electrons 0.84*4=4.2μ_B. It can be inferred as two holes located on two oxygen atoms, corresponding to the two proceeding deprotonations from the neutral *OH intermediate, without effecting the iron bulk like +3 oxidation state. The two holes on the oxygen atoms will induce later the creation of an O=O bond.

References

- 1 R. Birss, *Symmetry and magnetism*, 1964.
- 2 E. Zolotoyabko, *Basic Concepts of Crystallography: An Outcome from Crystal Symmetry*, 2011.