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Oxygen evolution reaction (OER) mechanism under alkaline and acidic conditions

Qiuhua Liang[1] , Geert Brocks[2,3,4] and Anja Bieberle-Hütter[1,2]

1 Electrochemical Materials and Interfaces (EMI), Dutch Institute for Fundamental Energy Research (DIFFER), De Zaale 20, 5612 AJ Eindhoven, The Netherlands
2 Center for Computational Energy Research (CCER), P.O. Box 513, 5600 MB Eindhoven, The Netherlands
3 Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
4 Computational Materials Science, Faculty of Science and Technology and MESA, Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

E-mail: A.Bieberle@differ.nl

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Abstract

Density functional theory (DFT) simulations of the oxygen evolution reaction (OER) are considered essential for understanding the limitations of water splitting. Most DFT calculations of the OER use an acidic reaction mechanism and the standard hydrogen electrode (SHE) as reference electrode. However, experimental studies are usually carried out under alkaline conditions using the reversible hydrogen electrode (RHE) as reference electrode. The difference between the conditions in experiment and calculations is then usually taken into account by applying a pH-dependent correction factor to the latter. As, however, the OER reaction mechanisms under acidic and under alkaline conditions are quite different, it is not clear *a priori* whether a simple correction factor can account for this difference. We derive in this paper step by step the theory to simulate the OER based on the alkaline reaction mechanism and explain the OER process with this mechanism and the RHE as reference electrode. We compare the mechanisms for alkaline and acidic OER catalysis and highlight the roles of the RHE and the SHE. Our detailed analysis validates current OER simulations in the literature and explains the differences in OER calculations with acidic and alkaline mechanisms.

1. Introduction

The oxygen evolution reaction (OER) is often regarded as the main bottleneck in water splitting due to its slow kinetics, which limits the efficiency of the energy conversion [1, 2]. During the last few decades, extensive studies have been devoted to the development and understanding of the OER [2–4]. Based on density functional theory (DFT) calculations, the OER mechanism under acidic conditions has been widely investigated [5–7]. However, most of the experimental studies are done in alkaline media instead of acidic media [8–10]. Although some computational papers consider OER calculations under alkaline conditions, the underlying theory from reaction mechanism to free energy equations is not made transparent and not derived explicitly [11–14]. Considering the dissimilarity between the computational and experimental approaches, it is crucial to derive the equations for DFT calculations of the OER with an alkaline mechanism explicitly and to compare the outcome to the acidic mechanism.

The widely accepted OER mechanism consists of four-electron/proton transfer steps in both acidic and alkaline media [3, 4, 14]. The OER is highly pH-sensitive; under acidic conditions, water molecules (H_2O) are oxidized, and $H^+ + e^-$ pairs and oxygen molecules (O_2) are released [3, 4]. In contrast, under alkaline conditions, hydroxyl groups (OH^-) are oxidized to H_2O and O_2 with concomitant release of e^- [14, 15]. In the literature, many theoretical studies assume an acidic mechanism for calculations of the catalytic activity of the OER of typical catalysts, such as Fe_2O_3 [5, 6], Co_3O_4 [10, 16], and Ni_3S_2 [17]. The catalytic activity for OER is typically characterized by calculating the Gibbs free energies of the individual reaction steps using the standard hydrogen electrode (SHE) as a reference electrode.

The acidic mechanism involves the production of $H^+ + e^-$ pairs, and their Gibbs free energy is usually calculated implicitly by assuming the equilibrium $H^+ + e^- \leftrightarrow 1/2H_2$ at standard conditions (pH = 0, pressure $p_{H_2} = 1$ bar, and $T = 298.15$ K) and using the Gibbs free energy of hydrogen gas [3, 4]. At a pH different from 0, the Gibbs free energy of H^+ ions can be corrected by the concentration dependence of the entropy, $k_B T \times$ pH $\times$ ln10 [3, 4]. The why and how of this correction factor has not been universally picked up in the literature and the step from the acidic to the alkaline reactions is not taken explicitly.

The alkaline mechanism involves the oxidation of OH^- with concomitant release of e^-. Therefore, calculating the Gibbs free energies of OH^- and e^- is crucial in order to characterize the OER under alkaline conditions. Some papers claimed that the calculation of the Gibbs free energies of OH^- and e^- can be obtained from the Gibbs free energy of $H^+ + e^-$, but how to deal with the free energy of $H^+ + e^-$ at a pH different from 0 is not thoroughly discussed.

Using the computational hydrogen electrode (CHE) approach developed by Bagger *et al* [18], the calculation of the free energy of $H^+ + e^-$ at a pH different from 0 can formally be solved by taking the reversible hydrogen electrode (RHE) as the reference electrode. Besides, in contrast to the SHE, the RHE is also generally used as reference electrode in experiments [8, 15]. The main advantage of using the RHE as reference electrode is that it equals the Gibbs free energy of $H^+ + e^-$ to the energy of $1/2H_2$ at arbitrary pH ($p_{H_2} = 1$ bar and $T = 298.15$ K) [19].
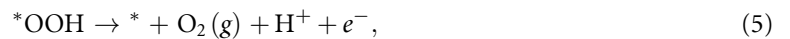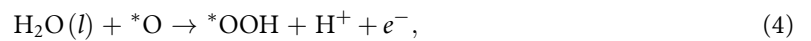
In this paper, we compare the OER mechanism under acidic and alkaline conditions starting explicitly from the corresponding reactions and the species involved. We derive the theory required to couple the results of DFT calculations to experiment (but actual DFT calculations are not discussed). The reaction steps, their Gibbs free energies, and the overpotential are explained separately for both these cases. Besides, we demonstrate the connection between the OER calculations that use the RHE and the SHE reference electrodes and explain in detail how the correction to the Gibbs free energy of H^+ ions at a pH different from 0 enters in the energy balance and in the overpotential.

2. OER using an acidic reaction mechanism

We consider a four-electron reaction mechanism for OER. Under acidic conditions, the overall water oxidation reaction is [3, 4, 20]

$$2H_2O\,(l) \rightarrow O_2 + 4H^+ + 4e^-; \quad \Delta G_0 = 4.92 \text{ eV} \tag{1}$$
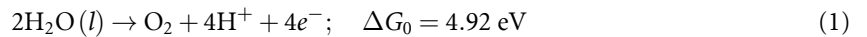
where (l) refers to the liquid phase. At $p = 1$ bar and $T = 298.15$ K, the Gibbs free energy difference $\Delta G_0 = 4.92$ eV for this reaction. The reaction is generally believed to proceed in four steps [3, 4, 20]

$$H_2O\,(l) + {}^* \rightarrow {}^*OH + H^+ + e^-, \tag{2}$$

$$^*OH \rightarrow {}^*O + H^+ + e^-, \tag{3}$$

$$H_2O\,(l) + {}^*O \rightarrow {}^*OOH + H^+ + e^-, \tag{4}$$

$$^*OOH \rightarrow {}^* + O_2\,(g) + H^+ + e^-, \tag{5}$$

where * represents the active site of the catalyst, (g) refers to the gas phase, and $^*OH$, $^*O$, and $^*OOH$ represent the species adsorbed on the active site. As explained in the previous section, at standard conditions, the Gibbs free energy of $H^+ + e^-$ equals the Gibbs free energy of $1/2H_2$. The reaction Gibbs free energies, which provide the binding strength between the catalyst and OER intermediates, are affected by the electronic properties of the active site. The typical procedure widely used in the literature to calculate the reaction Gibbs free energies, $\Delta G'_n$ corresponding to equations (2)–(5) at standard conditions [6, 20], is shown in equations (6)–(9); more details about the derivation can be found in [20].

$$\Delta G'_1 = E_{^*OH} - E_{^*} - E_{H_2O} + \frac{1}{2}E_{H_2} + (\Delta ZPE - T\Delta S)_1 - eU_{SHE}, \tag{6}$$

$$\Delta G'_2 = E_{^*O} - E_{^*OH} + \frac{1}{2}E_{H_2} + (\Delta ZPE - T\Delta S)_2 - eU_{SHE}, \tag{7}$$

$$\Delta G'_3 = E_{^*OOH} - E_{^*O} - E_{H_2O} + \frac{1}{2}E_{H_2} + (\Delta ZPE - T\Delta S)_3 - eU_{SHE}, \tag{8}$$

$$\Delta G'_4 = E_* - E_{*OOH} + \left(2E_{H_2O} - \frac{3}{2}E_{H_2}\right) + 4.92 + (\Delta ZPE - T\Delta S)_4 - eU_{SHE}, \tag{9}$$

where E_*, E_{*OH}, E_{*O}, E_{*OOH} are the total energies of the clean surface (*) and of surfaces with the single adsorbed species OH, O, and OOH, respectively, and E_{H_2O} and E_{O_2} are the total energies of the H_2O and O_2 molecules, all obtained from DFT calculations. ΔZPE and ΔS are the changes in vibrational zero-point energy and entropy from the initial state to the final state, respectively; T is temperature. In addition, ΔS contains the contributions of the gas and liquid phases used in reactions (2)–(5). U_{SHE} is the electrode potential relative to the SHE. $(\Delta ZPE - T\Delta S)_n$ $(n = 1, 2, 3, 4)$ can be calculated as:

$$(\Delta ZPE - T\Delta S)_1 = (ZPE_{*OH} - TS_{*OH}) - (ZPE_{H_2O} - TS_{H_2O}) + \frac{1}{2}(ZPE_{H_2} - TS_{H_2}), \tag{10}$$

$$(\Delta ZPE - T\Delta S)_2 = (ZPE_{*O} - TS_{*O}) - (ZPE_{*OH} - TS_{*OH}) + \frac{1}{2}(ZPE_{H_2} - TS_{H_2}), \tag{11}$$

$$(\Delta ZPE - T\Delta S)_3 = (ZPE_{*OOH} - TS_{*OOH}) - (ZPE_{*O} - TS_{*O}) - (ZPE_{H_2O} - TS_{H_2O}) + \frac{1}{2}(ZPE_{H_2} - TS_{H_2}), \tag{12}$$

$$(\Delta ZPE - T\Delta S)_4 = -(ZPE_{*OOH} - TS_{*OOH}) + 2(ZPE_{H_2O} - TS_{H_2O}) - \frac{3}{2}(ZPE_{H_2} - TS_{H_2}), \tag{13}$$

Therefore, the sum of change of the ZPE terms and the TS terms during the reaction cycle equals 0:

$$(\Delta ZPE - T\Delta S)_1 + (\Delta ZPE - T\Delta S)_2 + (\Delta ZPE - T\Delta S)_3 + (\Delta ZPE - T\Delta S)_4 = 0, \tag{14}$$

The reaction Gibbs free energies of equations (6)–(9) have to obey the sum rule.

$$\Delta G'_1 + \Delta G'_2 + \Delta G'_3 + \Delta G'_4 = \Delta G_0 - 4eU_{SHE}, \tag{15}$$

The overpotential is then given by

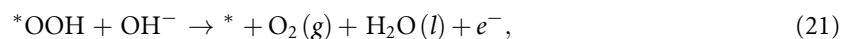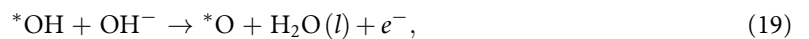$$\eta' = \frac{1}{e} \max_{n=1,2,3,4} [\Delta G'_n] - U_0. \tag{16}$$

where $U_0 = \Delta G_0/4e = 1.23$ V is the equilibrium potential, which is independent of pH and defined at $p = 1$ bar and $T = 298.15$ K. U_0 is the minimum potential required to run the reaction (1). Any reaction step (2)–(4) that has $\Delta G'_n/e > U_0$ requires a higher potential to run it, and the maximum $\Delta G'_n/e$ then defines the overpotential required for the whole four-step reaction to proceed.

3. OER using an alkaline reaction mechanism

Unlike under acidic conditions, equation (1), the water oxidation reaction under alkaline conditions is given by [14, 15]

$$4OH^- \rightarrow O_2(g) + 2H_2O(l) + 4e^-, \tag{17}$$
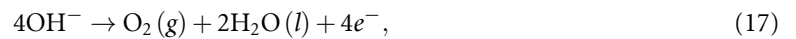
This reaction is usually assumed to proceed in four elementary steps [11]

$$^* + OH^- \rightarrow {}^*OH + e^-, \tag{18}$$

$$^*OH + OH^- \rightarrow {}^*O + H_2O(l) + e^-, \tag{19}$$

$$^*O + OH^- \rightarrow {}^*OOH + e^-, \tag{20}$$

$$^*OOH + OH^- \rightarrow {}^* + O_2(g) + H_2O(l) + e^-, \tag{21}$$

where the notation is the same as in equations (2)–(5). Different from the acidic mechanism, the Gibbs free energies of equations (18)–(21) are not commonly discussed. Thus, we would like to derive the theory for the

OER under alkaline conditions step by step. The reaction Gibbs free energies corresponding to equations (18)–(21) can be expressed as

$$\Delta G_1 = \mu_{*\text{OH}} - \mu_* - (\mu_{\text{OH}^-} - \mu_{e^-}), \tag{22}$$

$$\Delta G_2 = \mu_{*\text{O}} + \mu_{\text{H}_2\text{O}(l)} - \mu_{*\text{OH}} - (\mu_{\text{OH}^-} - \mu_{e^-}), \tag{23}$$

$$\Delta G_3 = \mu_{*\text{OOH}} - \mu_{*\text{O}} - (\mu_{\text{OH}^-} - \mu_{e^-}), \tag{24}$$

$$\Delta G_4 = \mu_* + \mu_{\text{O}_2(g)} + \mu_{\text{H}_2\text{O}(l)} - \mu_{*\text{OOH}} - (\mu_{\text{OH}^-} - \mu_{e^-}), \tag{25}$$

where μ are the (electro)chemical potentials of the indicated species. These chemical potentials can be obtained from [20]

$$\mu_* = E_*, \tag{26}$$

$$\mu_{*\text{OH}} = E_{*\text{OH}} + \text{ZPE}_{*\text{OH}} - TS_{*\text{OH}}, \tag{27}$$

$$\mu_{*\text{O}} = E_{*\text{O}} + \text{ZPE}_{*\text{O}} - TS_{*\text{O}}, \tag{28}$$

$$\mu_{*\text{OOH}} = E_{*\text{OOH}} + \text{ZPE}_{*\text{OOH}} - TS_{*\text{OOH}}, \tag{29}$$

$$\mu_{\text{H}_2\text{O}(l)} = E_{\text{H}_2\text{O}} + \text{ZPE}_{\text{H}_2\text{O}} - TS_{\text{H}_2\text{O}(l)}, \tag{30}$$

where E_* and E_{*X} are the (DFT) total energies of the clean surface (*) and of surfaces with a single adsorbed species X, respectively, and ZPE_{*X}, S_{*X} are the corresponding vibrational zero point energy and entropy. $E_{\text{H}_2\text{O}}$ is the total energy of the H_2O molecule, $\text{ZPE}_{\text{H}_2\text{O}}$ and $S_{\text{H}_2\text{O}(l)}$ the corresponding vibrational zero point energy and entropy contributions, where the latter also contains the free energy correction for the liquid state.

For O_2, the chemical potential is obtained from the experimental formation energy of O_2 with respect to water, since the O_2 molecule is not very well described within DFT. Assuming the equilibrium $\text{O}_2(g) + 2\text{H}_2(g) \leftrightarrow 2\text{H}_2\text{O}(l)$, the chemical potential of O_2 can be written as [20]

$$\mu_{\text{O}_2(g)} = 2G_{\text{H}_2\text{O}(l)} + \Delta G_0 - 2G_{\text{H}_2(g)}, \tag{31}$$

The only unknowns remaining in equations (22)–(25) are now μ_{OH^-} and μ_{e^-}, the chemical potentials of the OH$^-$ species and the electron, respectively, where we actually only need the difference $\mu_{\text{OH}^-} - \mu_{e^-}$. To calculate this difference, we assume the equilibrium

$$\text{H}_2\text{O}(l) \leftrightarrow \text{H}^+ + \text{OH}^-, \tag{32}$$

which relates the chemical potentials as

$$\mu_{\text{OH}^-} + \mu_{\text{H}^+} = \mu_{\text{H}_2\text{O}(l)}, \tag{33}$$

Using the trick

$$\mu_{\text{OH}^-} - \mu_{e^-} + \mu_{\text{H}^+} + \mu_{e^-} = \mu_{\text{H}_2\text{O}(l)}, \tag{34}$$

one can rewrite this as

$$\mu_{\text{OH}^-} - \mu_{e^-} = \mu_{\text{H}_2\text{O}(l)} - (\mu_{\text{H}^+} + \mu_{e^-}), \tag{35}$$

Here, $\mu_{\text{H}_2\text{O}(l)}$ can be calculated according to equation (30) and $(\mu_{\text{H}^+} + \mu_{e^-})$ can be calculated using the CHE approach [4, 18], where one assumes the equilibrium

$$\text{H}^+ + e^- \leftrightarrow \frac{1}{2}\text{H}_2(g). \tag{36}$$

We describe this equilibrium using the RHE as reference electrode, which operates under standard conditions of hydrogen gas pressure $p_{H_2} = 1$ bar and $T = 298.15$ K (but with a pH of the actual experimental conditions, which is different from zero), so

$$\mu_{H^+} = \mu_{H^+}^{RHE}, \tag{37}$$

The remaining electrochemical potential of the electrons can then be expressed as

$$\mu_{e^-} = \mu_{e^-}^{RHE} - eU_{RHE}, \tag{38}$$

where U_{RHE} is the potential of the electrode relative to the RHE [18].
Combining equations (36)–(38), the equilibrium can then be expressed as

$$\mu_{H^+} + \mu_{e^-} = \mu_{H^+}^{RHE} + \mu_{e^-}^{RHE} - eU_{RHE} = \frac{1}{2}\mu_{H_2(g)} - eU_{RHE}, \tag{39}$$

Substituting the equation (39) into equation (35), we finally have

$$\mu_{OH^-} - \mu_{e^-} = \mu_{H_2O(l)} - \left(\frac{1}{2}\mu_{H_2(g)} - eU_{RHE}\right), \tag{40}$$

Using equation (40) in equations (22)–(25) we get

$$\Delta G_1 = \mu_{*OH} - \mu_* - \mu_{H_2O(l)} + \frac{1}{2}\mu_{H_2} - eU_{RHE}, \tag{41}$$

$$\Delta G_2 = \mu_{*O} - \mu_{*OH} + \frac{1}{2}\mu_{H_2} - eU_{RHE}, \tag{42}$$

$$\Delta G_3 = \mu_{*OOH} - \mu_{*O} - \mu_{H_2O(l)} + \frac{1}{2}\mu_{H_2} - eU_{RHE}, \tag{43}$$

$$\Delta G_4 = \mu_* - \mu_{*OOH} + \mu_{O_2(g)} + \frac{1}{2}\mu_{H_2} - eU_{RHE}, \tag{44}$$

Applying equations (26)–(31) to equations (41)–(44), the final expressions for the reaction Gibbs free energies using an alkaline reaction mechanism become

$$\Delta G_1 = E_{*OH} - E_* - E_{H_2O} + \frac{1}{2}E_{H_2} + (\Delta ZPE - T\Delta S)_1 - eU_{RHE}, \tag{45}$$

$$\Delta G_2 = E_{*O} - E_{*OH} + \frac{1}{2}E_{H_2} + (\Delta ZPE - T\Delta S)_2 - eU_{RHE}, \tag{46}$$

$$\Delta G_3 = E_{*OOH} - E_{*O} - E_{H_2O} + \frac{1}{2}E_{H_2} + (\Delta ZPE - T\Delta S)_3 - eU_{RHE}, \tag{47}$$

$$\Delta G_4 = E_* - E_{*OOH} + \left(2E_{H_2O(l)} - \frac{3}{2}E_{H_2}\right) + \Delta G_0 + (\Delta ZPE - T\Delta S)_4 - eU_{RHE}, \tag{48}$$

The reaction Gibbs free energies of equations (45)–(48) obey the sum rule

$$\Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 = \Delta G_0 - 4eU_{RHE}, \tag{49}$$

and the overpotential is given by

$$\eta = \frac{1}{e} \max_{n=1,2,3,4} [\Delta G_n] - U_0. \tag{50}$$

4. Comparison between the acidic and the alkaline reaction mechanism

Under acidic conditions, the Gibbs free energy of $H^+ + e^-$ is linked to the Gibbs free energy of $1/2 H_2$ and the reaction Gibbs free energies are calculated from equations (6)–(9). Under alkaline conditions, the Gibbs free energy of $OH^- - e^-$ can be related to the Gibbs free energy of $H^+ + e^-$ according to equations (35) and (40). The reaction Gibbs free energies for the alkaline reaction mechanism can then be calculated from equations (45)–(48).

Comparing the reaction Gibbs free energies of the acidic (equations (6)–(9)) and of the alkaline (equations (45)–(48)) reaction mechanisms, it can be seen that the only difference lies in the electrode potential. In the case of the acidic mechanism, the electrode potential is related to the SHE and in the case of the alkaline mechanism, it is related to the RHE. Hence, the reaction Gibbs free energies can be calculated with almost the same equations even though the reaction mechanisms for the acidic environment, equations (2)–(5), and for the alkaline environment, equations (18)–(21), are different.

The equations used for calculating the overpotential, equations (16) and (50) are exactly the same. The numerical results will of course be different, as two different reference potentials, SHE and RHE, are used to calculate the Gibbs free energies in the acidic and the alkaline cases. The electrode potential of the two reference potentials can be linked according to [18]

$$eU_{RHE} = eU_{SHE} - k_B T \ln a_{H+} = eU_{SHE} + k_B T \times pH \times \ln 10. \quad (51)$$

where a_{H+} is the activity of the H^+ ions in solution. Substituting equation (51) into equations (45)–(48), one obtains the reaction Gibbs free energies with the SHE as reference. At $T = 298.15$ K one has $k_B T \times pH \times \ln 10 \approx 0.059 \times pH$ eV.

Substituting equation (51) into equations (45)–(48) for the alkaline reaction mechanism, one obtains the same expression as given in [3, 4, 20] for the acidic reaction mechanism with the correction factor $k_B T \times pH \times \ln 10$. Therefore, at $pH = 0$, the reaction Gibbs free energies can be calculated according to equations (6)–(9), with the overpotential given by equations (16). At a pH different from 0, the reaction Gibbs free energy should be corrected with $k_B T \times pH \times \ln 10$. Alternatively, using RHE as reference electrode, the reaction Gibbs free energy can be calculated by equations (45)–(48) at arbitrary pH and the overpotential can be calculated by equations (50).

5. Summary

The OER mechanism under alkaline and acidic conditions are discussed and key parameters for the OER, such as the reaction Gibbs free energy and the overpotential, are derived for both reaction mechanisms. It is shown that—even though the single reactions look quite different—the same equations can be used for calculating these key parameters, provided the RHE is used as a universal reference. The effect of using different reference electrodes, i.e. RHE or SHE, on the equations for the key parameters is discussed. We suggest for the future to use for both acidic and alkaline mechanisms the RHE as a reference electrode. In that case, equations (45)–(50) can be used for calculating the reaction Gibbs free energies and the overpotential for the OER at all pH values for both acidic and alkaline mechanism.

Acknowledgments

ORCID iDs

Qiuhua Liang ⓘ https://orcid.org/0000-0002-5436-5203
Anja Bieberle-Hütter ⓘ https://orcid.org/0000-0001-8794-9312

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