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# Unraveling the Competition between the Oxygen and Chlorine Evolution Reactions in Seawater Electrolysis: Enhancing Selectivity for Green Hydrogen Production

Catherine Harvey, Simon Delacroix, Cédric Tard

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1           **Unraveling the Competition between the Oxygen and Chlorine**  
2           **Evolution Reactions in Seawater Electrolysis: Enhancing Selectivity**  
3           **for Green Hydrogen Production.**

4  
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13  
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15 Heterogeneous Electrocatalysts, Seawater

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1 **Abstract**

2 Selective oxidation of water without production of chlorine during the electrolysis of  
3 seawater is a critical impediment towards obtaining green hydrogen. Indeed,  
4 understanding the complex competitive mechanisms of oxygen and chlorine formation at  
5 the anode is an analytic challenge. An argument for direct seawater electrolysis is  
6 presented with a dissection of the complications that arise at the anode in the presence  
7 of seawater ionic constituents such as the chloride ion. Electrolyser system durability and  
8 the impact on the current and voltage efficiencies are discussed. Critical challenges at  
9 the anode under the acidic conditions of proton exchange membrane water electrolysis  
10 interrelate the thermodynamic and kinetic constraints of the oxygen evolution reaction  
11 (OER) and the chlorine evolution reaction (CER) to elucidate the heterogenous  
12 mechanisms of the OER and the CER and the crucial stability predicament under  
13 selective OER electrocatalysis. The selectivity circumstances resolved by Density  
14 Functional Theory computations shed insight onto the reaction conditions that select for  
15 the preferred OER adsorbate chemisorption on the surface and substantiates the  
16 observed overpotentials required for the OER and CER; experimental rotating ring disk  
17 electrode analysis further indicate competitive adsorption of OER and CER reactants  
18 under an assumed Langmuir isotherm model. Identifying the rate determining step and  
19 breaking the scaling relationship of the AEM OER pathway may both improve the stability  
20 of the catalyst and achieve lower OER overpotentials. Critical insight is given into  
21 designing the heterogeneous electrocatalyst structure with selective facets, additional  
22 point defects, and augmented active site density through single atom catalysts. An  
23 argument for the utilization of ruthenium for its high natural ubiquity and modulable  
24 valence states that can facilitate atomic configurations with optimal active site d-band  
25 center energies to promote selective adsorbate binding is presented. Studies of in-situ  
26 filtration of the chloride ion under acidic conditions highlight the utility of manganese oxide  
27 and silica; the augmentation of the conductivity through manipulation of polaronic  
28 interactions; and the design of heterogeneous electrocatalysts with self-healing  
29 characteristics demonstrated in select molecular catalysts that may decrease the  
30 overpotential of the OER and achieve selectivity. It is with the hope that these design  
31 strategies provide insights into future research efforts to uncover an electrocatalytic  
32 surface selective for OER evolution under the perilous acidic conditions and reveal an  
33 effective solution as serendipitous as the abundancy of a natural resource such as  
34 seawater.

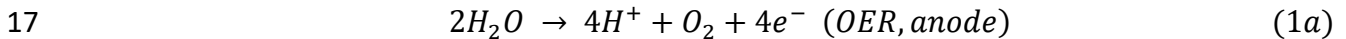
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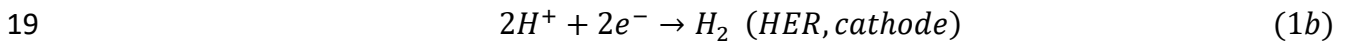
1 **I. Introduction**

2 I.1 The Social-Technological Crisis

3 Energy consumption is expected to reach 100,000 terawatt-hours (TWh) in the Net-Zero  
4 Emissions Scenario (NZES), outlined at the 2015 Paris agreement to minimize global  
5 temperature increases to 1.5 °C by the year 2050 [1,2]. This NZES expects water  
6 electrolysis to adsorb about 15,000 TWh to produce the required 520 mega tons of  
7 hydrogen to sustainably power our world [1,2]. Indeed, the generation of a hydrogen  
8 energy vector that is derived from renewable energy sources (“green hydrogen”) would  
9 fulfill the world's energy shortage while also evading these climatically harmful carbon  
10 emissions that warm the planet [3,4]. Water electrolysis was initially discovered by two  
11 Dutchmen, Adriann Paets van Troostwijk (1752–1837) and Johan Rudolph Deiman  
12 (1743–1808), who connected two gold wires to an electrostatic generator that were each  
13 placed at either end of a glass tube filled with water [5]. The electric discharges of the  
14 generator produced evolved gases on both wires. Those evolved gases were interpreted  
15 to be oxygen at the anode and hydrogen at the cathode, shown in the reactions below  
16 under acidic conditions.



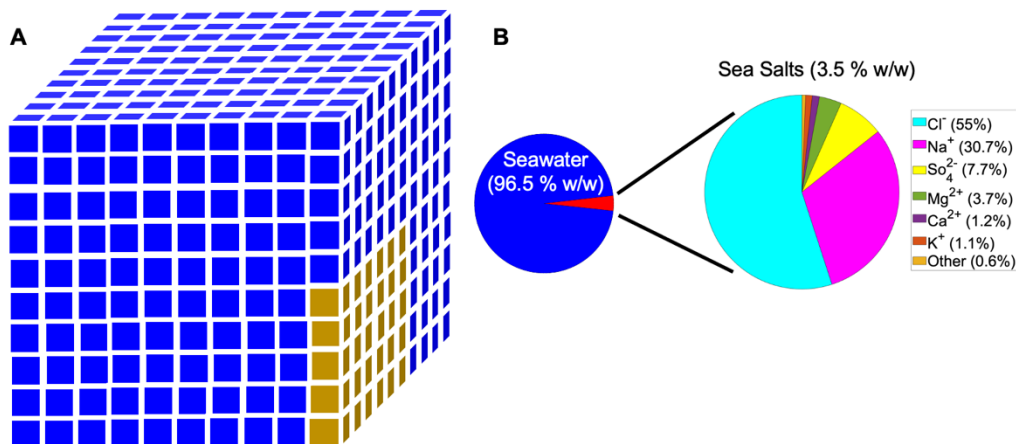
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20 Considering that the production of one ton of hydrogen requires about 10 m<sup>3</sup> of water,  
21 there will become an exigency to source and also transport upwards of 5,2 km<sup>3</sup> of water  
22 [6]. With total global renewable freshwater resources estimated at 49,809 × 10<sup>9</sup> m<sup>3</sup> in  
23 2020, exclusive withdrawals would dry up our critical freshwater resources within 100  
24 years [7]. Moreover, utilizing freshwater to power electrolysis would heighten the  
25 emerging social-technological crisis inherent in the water-energy nexus [8]. More than  
26 two billion people live in countries experiencing water stress and an estimated 1.6 billion  
27 people live in regions with water availability though without the infrastructure to access it  
28 [9]. Alleviating that social-technological crisis and propelling the sustainability of our  
29 society requires unlocking the other 96.5 % of the 1.69 × 10<sup>9</sup> km<sup>3</sup> of seawater water on  
30 earth portrayed in Fig. 1a.

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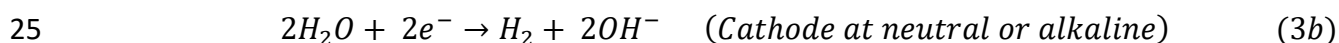
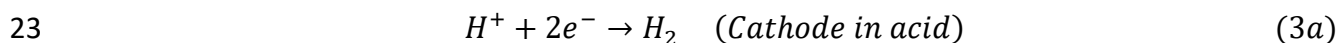
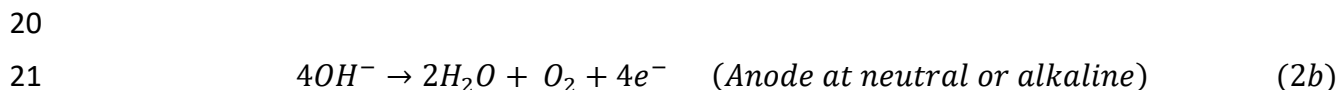
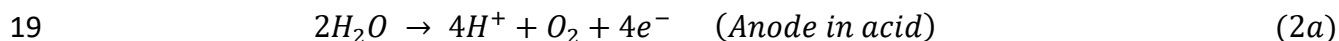


1  
 2 Fig. 1. (A) Graphical representation of the volumetric percentages of ice and seawater (97 % v/v) on the Earth  
 3 represented by blue squares and freshwater (3 % v/v) represented by gold squares, adapted from Urban [8]. (B)  
 4 Diagram of the major chemical constituents of seawater, sea salt percentages were adapted from the seawater  
 5 reference composition defined by Millero et al. and represent the mass fractions of the solute with respect to the total  
 6 mass of solutes at pH 8 [10].

7 However, there is plethora of chemical constituents in seawater including sea salts, small  
 8 organic molecules, living organisms, and polymers (Fig. 1b) which create complications  
 9 during the electrolysis [10,11]. Especially, one of the major challenges during the seawater  
 10 electrolysis is the presence of chlorine anions which induces a competition between  
 11 oxygen and chlorine production (CER).

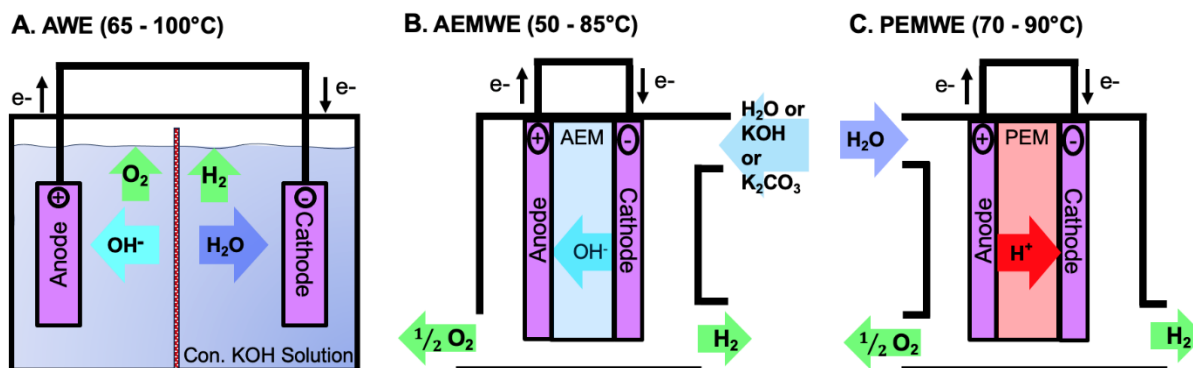
## 12 1.2. State-of-the-Art Water Electrolyser Technologies

13 Undergoing the preferential oxygen evolution reaction (OER) at the anode and the  
 14 hydrogen evolution reaction (HER) at the cathode leads to local acidification at the anode  
 15 as water or hydroxide ions are consumed under acidic or neutral/basic conditions and  
 16 protons or water are produced (*Reaction 2a* and *Reaction 2b*), and a local basification at  
 17 the cathode as protons or water molecules are consumed under acidic or neutral/basic  
 18 conditions and water or hydroxide ions are produced (*Reaction 3a* and *Reaction 3b*).



26  
 27 The pH dependence of the OER enables the reaction at the anode to evolve at voltages  
 28 below its characteristic reversible potential of  $1.23 \text{ V} - 0.059 \cdot \text{pH}$  vs. RHE in alkaline  
 29 solutions in accordance with the Nernst relation. Alkaline water electrolysis (AWE) utilizes  
 30 a cell with two compartments continuously fed with a highly concentrated, corrosive

1 alkaline supporting electrolyte (often 20–30 wt% (ca. 7 M) KOH solution), though this  
 2 design is subject to leakages and require periodic replenishment (Fig. 3a). The electrodes  
 3 are separated by a porous diaphragm to prevent gas crossover, though this diaphragm  
 4 has been shown to poorly operate, causing low Faradaic efficiencies, and limiting the  
 5 maximum AWE current densities to about 0.2 - 0.4 A/cm<sup>2</sup> despite the use of the highly  
 6 concentrated supporting electrolyte [12]. The device must also be operated at ambient  
 7 pressures, making the produced hydrogen significantly wet and increasing the cost of  
 8 drying and compression. Moreover, electrolysis of seawater under alkaline conditions can  
 9 induce hydroxide precipitation and reduce the lifetime durability of the electrolyser and  
 10 the active surface area of the electrocatalyst [13].



11  
 12 Fig. 2. (A) An alkaline water electrolyser with a concentrated KOH liquid supporting electrolyte pumped on both sides  
 13 of the cell with a porous diaphragm that impedes gas crossover while promoting the migration of the hydroxide ions  
 14 generated at the cathode toward the anode. (B) An anion exchange membrane water electrolyser consisting of a solid  
 15 cationic polymer promoting migration of hydroxide ions from the cathode to the anode where oxidation occurs; water  
 16 with or without a dilute supporting electrolyte such as potassium hydroxide or potassium carbonate is shown being  
 17 supplied to the cathode. (C) A proton exchange membrane water electrolyser with water being supplied to the anode;  
 18 the evolution of oxygen promotes the generation of protons that then migrate through the solid poly-sulfonic  
 19 membrane towards the cathode to evolve hydrogen. Reproduced from Li et al. [14].

20 Anion exchange membrane water electrolysis (AEMWE) utilizes an anion exchange solid  
 21 polymer electrolyte (< 50 μm in thickness). This membrane facilitates the transport of  
 22 hydroxide ions from the cathode to the anode and separates the evolved gases while  
 23 decreasing the ionic resistance. Thus AEMWE can operate at higher pressures with more  
 24 efficient current densities (Fig. 3b). Indeed, Li et al. reported current densities of 2.7  
 25 A/cm<sup>2</sup> using an ammonium-enriched anion exchange ionomer embedding both the  
 26 cathode and the anode [15]. To improve the ionic conductivity, dilute solutions of KOH (<  
 27 1 M) supporting electrolyte or potassium carbonate are often needed, though pure water  
 28 is preferred to minimize chemical and device maintenance. Water is indeed a feasible  
 29 electrolyte solution with an ionomer of sufficient cationic functionality and electrode  
 30 binding ability [12,14]. Moreover, the non-acidic environment enables the use of non-  
 31 precious metals electrocatalysts such as first-row transition metal oxides, nitrides, and  
 32 sulfides decreasing the capital expenditure, and increasing the scalability. Anion  
 33 exchange membranes can also enable the design of asymmetric electrolysers with  
 34 independent electrolyte feeds to promote the selectivity for the OER at the anode [16].  
 35 Dresp et al. developed an electrolyser where 0.5 M KOH anolyte circulate in the anode  
 36 compartment which was separated from natural seawater catholyte by an AEM  
 37 membrane. Only few millimole of chloride ion can cross over in the anolyte, unaffected

1 the NiFe-LDH electrocatalyst. In another study, a custom made biphenyl-based ionomer  
2 showed high anion exchange capacities contributing to low overpotential at high current  
3 densities [17].

4 The highest current densities are achieved with proton-exchange membrane water  
5 electrolyzers (PEMWE). In PEMWE, a solid polymer electrolyte membrane between the  
6 anode and the cathode such as Nafion is used to facilitate migration of the protons  
7 generated at the anode towards the cathode where their reduction occurs (Fig. 3c). This  
8 solid polymer allows for high operating pressures. However, it is especially vulnerable to  
9 water impurities, which can become trapped and concentrated, reducing the proton  
10 conductivity. Moreover, the harshly acidic conditions require the use of platinum group  
11 metals (PGM) such as iridium or ruthenium at the anode to catalyze the OER, and  
12 platinum or palladium HER catalysts at the cathode. The local acidification of the anode  
13 caused by the OER at high current densities may moreover increase the degradation of  
14 the electrode materials. Thus, it is crucial to develop acidic resistant catalysts to avoid  
15 continuous buffer additions [[18], [19], [20], [21]]. Unfortunately, the thermodynamic  
16 potential difference between the OER and the parasitic CER when electrolyzing seawater  
17 is the lowest under acidic conditions. To avoid the chlorine production, Rossi et al. use an  
18 asymmetric design electrolyte feed in which a humidified gas stream is introduced at the  
19 anode, while the chloride ions in the seawater catholyte were prevented from crossover  
20 by the electrostatic repulsions presented from the anionic functionalities of the membrane  
21 [22]. The vapor anolyte further reduced the occurrence of sodium ion transport and  
22 decreased the observed overpotentials of the cell [22]. Kumari et al. went one step further  
23 to introduce seawater humidified air at the anode and a nitrogen gas stream in the  
24 cathode compartment; the solar hydrogen conversion efficiency calculated before and  
25 after 50 h of continuous operation was found to increase from 6 % to 6.3 % compared to  
26 the decrease of 6.6 % to 0.5 % observed when liquid seawater electrolytes feeds were  
27 used [23].

#### 28 1.4.1 Abating the Use of Precious Metals in PEMWE

29 Krishnan et al. calculated an 82 % price reduction in the PEMWE stack design through  
30 alternative materials utilization and lower loadings of PGM electrocatalysts. Unfortunately,  
31 the high overpotential for the OER, the low pH contributed by the ionic membrane, and  
32 the highly oxygenated environment at the anode necessitates an electrocatalyst with a  
33 durability currently only characteristically found in iridium [24]. Though with loadings of 2  
34 mg/cm<sup>2</sup> required to achieve typical operating conditions of 2 A/cm<sup>2</sup> and 2 V, only a  
35 capacity of > 1 GW per year of PEMWE production technology can be achieved by  
36 tapping almost 10 % of the annually mined production [24]. Though to meet the NZES for  
37 2050, upwards of 3600 GW must be realized [24], thus ensuing an iridium shortage [25].  
38 On the other hand, costing a sixth to a fifteenth of the price of the extremely rare iridium  
39 metal with 0.001 ppm in the Earth's crust, both DFT studies and experimental  
40 measurements of its overpotential have rendered ruthenium as the precious metal with  
41 remarkable OER electrocatalytic activity under acidic conditions [26,27]. However, its  
42 preferential utilization must address its characteristically low stability.

43 Therefore, there exists a challenge to reduce the precious metal loadings without however  
44 sacrificing the performance and durability of the electrocatalyst. Alia et al. indeed showed  
45 that reduced metal loadings can degrade the current density over the long term [28]. Thus  
46 coherent strategies to diminish the precious metal loading are exigent. Improving the

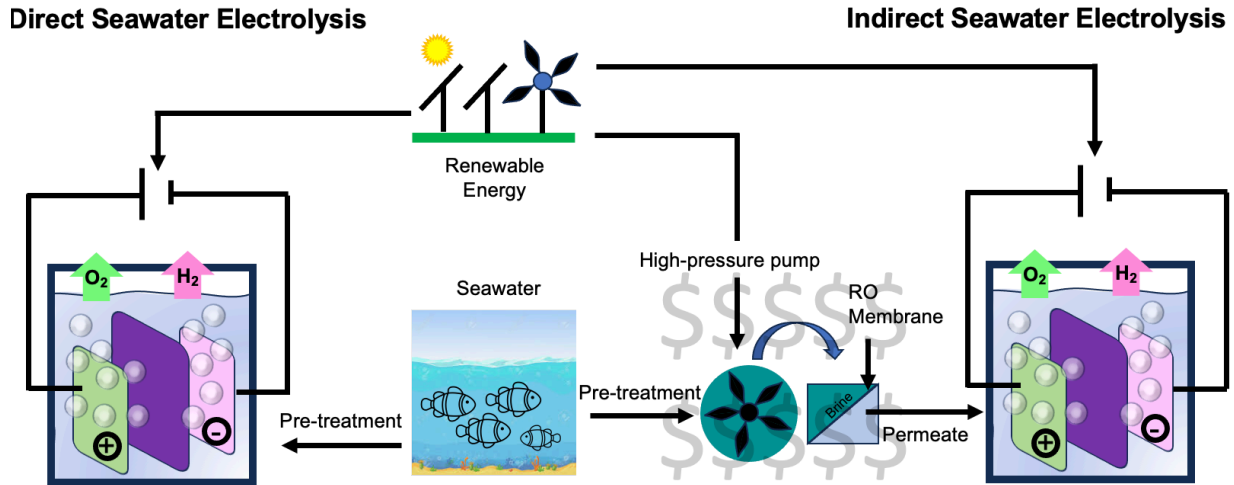


1 catalytic interface by incorporating supportive substrates with improved electrical  
2 conductivity; optimizing the surface area of the catalyst structure and iridium packing  
3 density by implementing the design of 1D and 2D nanomaterials; utilizing reactive spray  
4 deposition technologies with a self-assembly mechanism proceeding through volatile  
5 solvent evaporation that creates a porous hierarchical structure with low Ir loadings [29]  
6 are some methodologies that have been explored and discussed in the literature.  
7 Techniques that improve catalyst recycling such as ultrasonication and alcoholic  
8 delamination have also been reported [30,31].  
9 Development of non-PGM catalysts would evidently alleviate the cost burden of current  
10 PEM technology and the taxing utilization of precious natural resources. However, the  
11 lacking level of performance and durability of these alternatives when compared to Ir have  
12 continually rendered this feat elusive [24]. Towards assuaging this predicament, Wang et  
13 al. identified 68 nonbinary acid-stable oxides as electrocatalysts at the anode for PEMWE  
14 from the data of the Material Project through computation of Pourbaix decomposition free  
15 energies. For example, Sb, Ti, Sn, Ge, Mo, and W-based oxides were indicated to have  
16 high corrosion resistance in strong acids [32]. Moreover, Li et al. identified a stable  
17 potential window in which  $\gamma$ -MnO<sub>2</sub> showed no signs of deactivation after 8000 h of  
18 electrolysis at 10 mA/cm<sup>2</sup> and pH = 2 [33]. Hernandez et al. reported a nickel-manganese  
19 antimonate electrocatalyst that performed the OER in 1 M sulfuric acid, though required  
20 an overpotential of 735 mV operating at 10 mA/cm<sup>2</sup> for 168 h [34]. Thorarinsdottir et al.  
21 elucidated the OER catalytic mechanism of bismuth oxide (BiO<sub>x</sub>) films electrodeposited  
22 on fluorine-doped tin oxide-coated glass working electrodes and posited that two  
23 Bi<sup>3+</sup>O<sub>x</sub> centers undergo two sequential two-electron oxidations to form the symmetric  
24 peroxy Bi<sup>4+</sup>O<sub>x</sub>Bi<sup>4+</sup>O<sub>x</sub> entity, which then disproportionates intermolecularly to form a mixed  
25 valence Bi<sup>3+</sup>O<sub>x</sub>Bi<sup>5+</sup>O<sub>x</sub> peroxy species [35]. Upon oxidation to form Bi<sup>5+</sup>O<sub>x</sub>Bi<sup>5+</sup>O<sub>x</sub>, oxygen  
26 is subsequently released. No distinctive changes in film morphology were evident through  
27 SEM following chronopotentiometry testing; an OER current density of 1–5 mA/cm<sup>2</sup> was  
28 sustained at moderate overpotentials for 110 h at pH 1.82, acidified with sulfuric acid [35].  
29 These results further demonstrated that the p-block metal oxides often used as the  
30 stabilizing embedding matrices may indeed play a catalytic role in acidic OER  
31 electrocatalysis. On the other hand, an overpotential of 189 mV at 1 mA/cm<sup>2</sup> was  
32 recorded for a metal molecular cluster anion, a barium salt of cobalt polyoxometalate  
33 blended with a commercial carbon paste support; this design showed a stable current  
34 density for one day that was 10 times higher than that of iridium oxide (IrO<sub>2</sub>) blended with  
35 the carbon paste support, producing a TON of 47 compared to 0.1 for IrO<sub>2</sub> when corrected  
36 for the metal content. This was the first instance in which a low-cost, earth abundant  
37 material reached comparable activities to the commercial IrO<sub>2</sub> standard [36].

## 38 1.2 Indirect Seawater Electrolysis Technologies

39 The complexity of seawater instigates the development of new strategies to electrolyze  
40 this abundant resource to produce hydrogen. Desalination of seawater is currently used  
41 in electrolyser technologies and called indirect seawater electrolysis. Current desalination  
42 technologies include forward osmosis [37,38] and reverse osmosis (RO). RO occupied  
43 66 % of the global water desalination in 2016 and utilizes polyamide membranes capable  
44 of 99.7 % salt rejection [[39], [40], [41], [42]]. These relatively easy single reverse osmosis  
45 technologies can produce water with conductivities of 5–20  $\mu$ S/cm. However, the  
46 European Union recommends low temperature water electrolysis to be conducted

1 according to ISO 3696 Grade 2 water with a conductivity of  $< 1.0 \mu\text{S}/\text{cm}$   
 2 [[43], [44], [45], [46]]. Thus, the infrastructure for additional purification is required.  
 3 Reverse osmosis membranes could be placed in series, though each of these high  
 4 pressure pumps require 2 to 4 kWh of energy to produce  $1 \text{ m}^3$  of freshwater [47]. Purifying  
 5 the needed  $5.2 \text{ km}^3$  of water to meet the NZES could thus require 20.8 TWh of energy as  
 6 highlighted in Fig. 2. Thus it is of a fundamental importance to continue scientific  
 7 advancement into the development of direct seawater electrolysis to spare energy.



8  
 9 Fig. 3. Schematic comparison of Direct and Indirect Seawater Electrolysis highlighting the additional energy costs  
 10 required to power the high-pressure pump module. Figure adapted from Farràs et al. [48].

## 11 II. Mitigating Seawater Electrolyser Performance

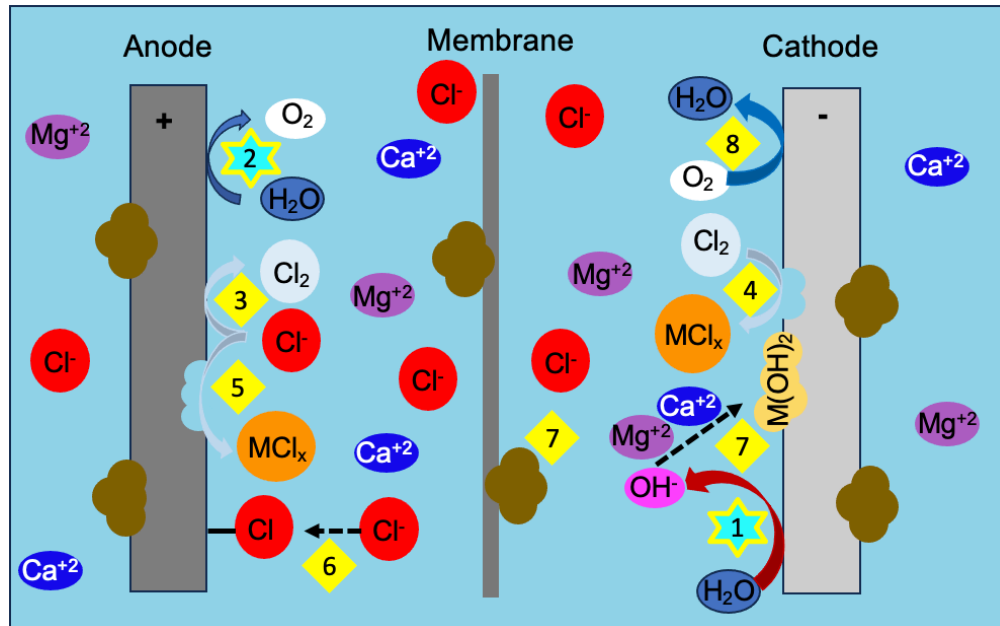
12 It is therefore crucial to be able to produce green hydrogen with direct electrolysis starting  
 13 from seawater. However, the presence of salts induces drop in performances.

### 14 II.1 Parasite Reactions in Seawater Electrolysers

15 The electrolysis of non-purified seawater has been shown to degrade the electrolyser  
 16 system performance. The carbonate and borate ions in seawater are present, though at  
 17 concentrations too low to buffer a seawater electrolyte from these dramatic pH shifts that  
 18 occur upon the preferential evolution of oxygen and hydrogen at the anode and the  
 19 cathode. The local acidification that occurs at the anode enables seawater constituents  
 20 such as the chlorine chemistry to promotes the corrosion and toxicity. The local  
 21 basification that occurs at the cathode causes hydroxide precipitation and the blockage  
 22 of the electrode surfaces and the membrane materials. This convoluted composition can  
 23 thus affect the chemical and mechanical robustness of the electrolyzer, the  
 24 electrochemically active dimensions of the electrode, and the specific operating  
 25 conditions (voltage, current density, solution feed rate, response time to reach steady-  
 26 state operation) [49].

27 Furthermore, the presence of additional chemical constituents into the electrolyte of the  
 28 electrolyser can create competition among the substrate at the active site of the  
 29 electrocatalyst [11,50]. In particular, the chloride ion can be oxidized at the anode  
 30 (**Reaction 3** of Fig. 4) in place of water to create toxic chlorine gas. After the CER, the  
 31 evolved chlorine or its disproportioned species can then travel to the cathode and be

1 reduced as shown in **Reaction 4** of Fig. 4 corroding the cathode. The chloride ions can  
 2 also replace the oxygen atoms in a passivated surface and cause pitting corrosion along  
 3 the anode, as shown in **Reaction 5** of Fig. 4 [[51], [52], [53], [54]]. The catalysts can also  
 4 become poisoned by the presence of these noninnocent ions, **Reaction 6** of Fig. 4.  
 5 [55,56].

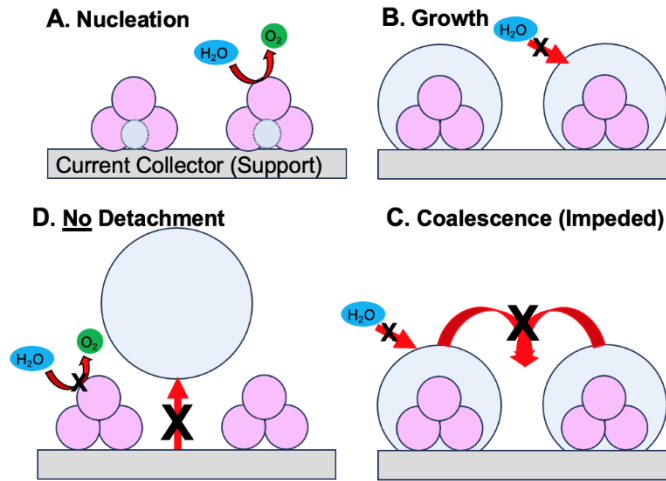


6  
 7 Fig. 4. Depictive representation of the inherent complications of seawater electrolysis. The desired efficiencies for the  
 8 HER (Reaction 1) and OER reactions (Reaction 2) can be undermined by the presence of antagonistic ions in the  
 9 electrolyte such as the chloride ion, which can compete with water to undergoes oxidation at the anode (Reaction 3).  
 10 The toxic chlorine gas and its disproportionation species can then undergo reduction at the cathode and corrode the  
 11 electrode (Reaction 4). The chloride ion can also corrode the anode by replacing the oxygens along the passivated  
 12 surface (Reaction 5). The ions can also inhibit the catalysts at the anode and cathode by affecting their functionality  
 13 and promoting dissolution (Reaction 6). The local basic environment of the cathode can also cause magnesium and  
 14 calcium hydroxides to precipitate and block the functionality of the electrocatalysts; these deposits can also become  
 15 trapped along the electrolyser membrane (Reaction 7). Parasitic oxygen reduction reactions can also occur at the  
 16 cathode (Reaction 8).

17 Other ions present in seawater can also affect the electrode integrity. The precipitation of  
 18 magnesium and calcium hydroxides, shown in **Reaction 7** of Fig. 4, lead to depositions  
 19 on the electrode surface that inhibit the functionality of the electrocatalysts [57,58]. These  
 20 magnesium and calcium hydroxide precipitates can also become trapped and  
 21 concentrated in electrolyser membranes, causing deactivation and reducing the lifetime  
 22 durabilities of these essential components [59]. Han et al. utilized a bipolar membrane  
 23 consisting of an anion exchange layer and a cation exchange layer under reverse bias to  
 24 promote local acidification in the catholyte to inhibit this inorganic precipitation [60]. Sadly,  
 25 this novel design decreases the susceptibility towards evolved O<sub>2</sub> which can cross toward  
 26 the membrane and induced a parasitic oxygen reduction reaction (**Reaction 8**, Fig. 4)  
 27 [11,50]. Finally, membranes could be subject to significant microbial fouling in presence  
 28 of seawater [61]. For example, Belila et al. found that 0.25 % of the bacterial operational  
 29 taxonomic units were present at all stages within a water desalination plant, and further  
 30 indicated that chlorination was not effective at inactivating all bacteria and preventing  
 31 microbial growth [62]. Though Debiemme-Chouvy and Cachet do suggest that

1 electrochemical methods such as the generation of hydrogen bubbles and a low-intensity  
 2 electrical potential may prevent the formation of a biofilm [63].

3 It worth to mention that all these precipitates and deposits decreases logically the  
 4 electrochemically active surface of the cell and stack components. In addition, gas  
 5 bubbles generated during the electrolysis of seawater may also be less prone to  
 6 coalesce than the ones in freshwater (Fig. 5) [64,65]. Tourneur et al. have however  
 7 recently found that the introducing cylindrical micropatterns at the surface of the  
 8 electrode can promote gas bubble release [66].



9  
 10 Fig. 5. Stages of gas bubble (grey) formation on an electrocatalytic nanoparticle (pink) along a conductive support  
 11 beginning with (A) nucleation followed by (B) growth. Seawater impedes the coalescence of the bubbles (C) preventing  
 12 the electrocatalytic material from oxidizing (or reducing) adjacent water molecules (D).

### 13 II.3 Drop in the Electrolyzer Efficiency using Seawater

14 The efficiency of the individual cells may be determined as a product of the current  
 15 efficiency ( $\tilde{\eta}_C$ ) and the voltage efficiency ( $\tilde{\eta}_U$ ), which includes the power consumption to  
 16 maintain the heat balance during endothermic and exothermic electrode processes and  
 17 prevent potential electrolyte freezing and elevated temperatures [67]. All the parameters  
 18 influencing the efficiency are listed in Table 1 (adapted from Schalenbach et. Al) [77].

19 
$$\tilde{\eta}_{cell} = \tilde{\eta}_C * \tilde{\eta}_U \quad (4)$$

20 Table 1. Classification of the operational parameters, electrolyte characteristics, and properties of the electrocatalyst  
 21 and the electrodes that affect the voltage efficiency, the current efficiency, the heat balance, and thus the overall cell  
 22 efficiency. Adapted from the work of Schalenbach et al. [67].

23  
 24  
 25  
 26  
 27  
 28  
 29  
 30  
 31

	Cell efficiency		
	Voltage efficiency	Current efficiency	Heat balance
Operation parameters	Temperature Pressure Cell current	Temperature Pressure Cell current	Temperature Pressure Cell current
Electrolyte	Membrane thickness Conductivity	Membrane thickness Diffusivities Permeabilities	Membrane thickness Vapor pressure
Catalyst and electrodes	Morphology Permeability Activity Surface area Conductivity	Morphology Permeability	

### 1 II.3.1 The Current Efficiency

2 The current efficiency ( $\tilde{\eta}_c$ ) also known as a faradaic efficiency, is the ratio between the  
3 moles of hydrogen produced ( $\Delta n_{H_2}$ ) to the moles of electrons used during the electrolysis  
4 process ( $\Delta n_{e^-}$ ). The current efficiency can be given by the following equation:

$$5 \quad \tilde{\eta}_c = \frac{\Delta n_{H_2}}{\Delta n_{e^-}} = \frac{\frac{I\Delta t}{2F} - \Delta n_{loss}}{\frac{I\Delta t}{2F}} = \frac{I - 2F\left(\frac{\Delta n_{loss}}{\Delta t}\right)}{I} = \frac{I - I_{loss}}{I} \quad (5)$$

6 Where (I) is the current, (t) is the time, and (F) is Faraday's constant.

7 Current efficiencies at the anode and cathode are affected by two major losses. The first  
8 one is the recombination of H<sub>2</sub> and O<sub>2</sub> in H<sub>2</sub>O and the second one is the current loss  
9 caused by the parasitic CER. The recombination of H<sub>2</sub> and O<sub>2</sub> is caused by the diffusion  
10 of the gases through the membrane and the convection insured by the electrolyte of the  
11 solubilized gases through the membrane [67]. Thus,  $I_{loss}$  can be written as following:

$$12 \quad I_{loss} = I_{loss}^{recombination} + I_{loss}^{CER} \quad (6a)$$

$$13 \quad I_{loss} = 2F\left(\frac{K}{\mu}p_c^{H_2} - D_{H_2}\right)S_{H_2}\frac{\Delta p}{d} + 4F\left(\frac{K}{\mu}p_a^{O_2} - D_{O_2}\right)S_{O_2}\frac{\Delta p}{d} + I_{loss}^{CER} \quad (6b)$$

14

15 Gordon et al. reported the solubility of hydrogen at various salinities of local seawater  
16 samples. They found the hydrogen solubility to decrease with increasing salinity [68].

1 Thus, differences in hydrogen diffusivity and permeability through the membrane are  
2 expected to affect the cross-permeation flux densities.

### 3 II.3.2 The Voltage Efficiency

4 The voltage efficiency,  $\tilde{\eta}_U$ , can be defined with respect to the reversible voltage of a water  
5 electrolytic cell ( $U_{rev,T}$ ) and the applied voltage ( $U_{cell}$ ). These two parameters are affected  
6 by the use of seawater.

$$7 \quad \tilde{\eta}_U = \frac{U_{rev,T}}{U_{cell}} \quad (7)$$

8 The reversible voltage ( $U_{rev,T}$ ) is affected by the presence of salts in water. Indeed,  
9 increasing the salinity of the aqueous electrolyte solution is known to lower its  
10 characteristic vapor pressure ( $p_w$ ) at a total pressure ( $p$ ) [69]. By assuming that the water  
11 vapor is ideal and in equilibrium with the water in its electrolyte solution at a vapor  
12 pressure ( $p_w^*$ ), the effect of this vapor pressure on the reversible voltage of a water  
13 electrolytic cell  $U_{rev,T,p}$  at temperature ( $T$ ) may be defined as following [70]:

$$14 \quad nFU_{rev,T,p} = nFU_{rev,T}^\circ + RT \ln \left[ \frac{(p - p_w)^{3/2} \cdot p_w^*}{p_w p^{1/2}} \right] \quad (8)$$

15 Where the Nernst relation with the standard reversible voltage ( $U_{rev,t}^\circ$ ) may be equated to  
16 the standard free energy of formation of liquid water, which at 25°C is  $-2.37 \times 10^5$  J, giving  
17 ( $U_{rev,t}^\circ$ ) a value of 1.229 V.

18 The applied cell voltage ( $U_{cell}$ ) is also modified by the use of seawater. Indeed, ( $U_{cell}$ ) is  
19 defined as the sum of the Nernst voltage  $U_N$ , the ohmic drop  $U_\Omega$ , and the kinetic  
20 overpotential  $U_{kin}$  [67].

$$21 \quad U_{cell} = U_N + U_\Omega + U_{kin} \quad (9)$$

22  
23  
24  $U_N$  is affected by the partial pressure ( $p_{H_2}^C$ ) and ( $p_{O_2}^A$ ) at the cathode and anode,  
25 respectively. Assuming that the gaseous hydrogen and oxygen produced at the  
26 electrodes are saturated with the water vapor, we obtained the following expression for  
27  $U_N$ .

$$28 \quad U_N = U_{rev,T}^\circ + \frac{RT}{2F} \ln \left( \frac{p_{H_2}^C \sqrt{p_{O_2}^A}}{p^{3/2} a_{H_2O}} \right) \quad (10)$$

29 Where  $R$  is the universal gas constant,  $T$  is the temperature, ( $a_{H_2O}$ ) is the activity of water,  
30 ( $p_{H_2}^C$ ) and ( $p_{O_2}^A$ ) represent the partial pressures of hydrogen and oxygen at the cathode  
31 and anode, respectively, and ( $p$ ) denotes the ambient total pressure as used above.

32 However, depending on the pH of the solution, only the proton and/or hydroxide ions  
33 involved in the oxidation and reduction reactions of water electrolysis that evolve the

1 measured stationary currents at the anode and the cathode can contribute to the specific  
 2 conductance ( $K_s$ ) of the electrolyte [67]. Seawater alone is known to have a lower specific  
 3 conductance than the buffered osmotic water used in PEMWE or AWE technologies.  
 4 Electrolyzing seawater alone will thus require a greater applied cell voltage ( $U_{cell}$ ) due the  
 5 increase in the Ohmic drop ( $U_{\Omega}$ ), of the cell by increasing the total DC resistance between  
 6 the cathode and the anode ( $R_t$ ), which affects the overall voltage efficiency of the  
 7 electrolyzer [71].

$$8 \quad U_{\Omega} = R_t j \quad (11a)$$

$$9 \quad R_t = \frac{1}{K_s} \quad (11b)$$

### 10 *II.3.2.1 A Consideration for the heat flow.*

11 It is desirable for electrolyzers to operate at a fixed temperature. Leroy et. al. defined the  
 12 thermobalanced voltage ( $U_{TB}$ ) by considering the heat of vaporization ( $T\Delta S$ ) caused by  
 13 the phase transition of liquid water to gaseous oxygen and hydrogen, the heat of  
 14 vaporization ( $H_{ev}^{gas}$ ) that accounts for the phase transition of liquid water into gaseous  
 15 water vapor, and the energy required to increase the temperature of the supply water at  
 16 ambient temperature (20 °C) to typical cell temperatures of 80 °C ( $E_{Supply}$ ),

$$17 \quad U_{TB} = U_{rev,T}^{\circ} + \frac{T\Delta S}{2F} + \frac{E_{Supply}}{2F} + \frac{H_{ev}^{gas}}{2F} \quad (12)$$

18 The voltage efficiency can thus be further defined.

$$19 \quad \tilde{n}_U = \frac{U_{rev}}{U_{TB}} \text{ for } U_{cell} \leq U_{TB} \quad (13a)$$

$$20 \quad \tilde{n}_U = \frac{U_{rev}}{U_{cell}} \text{ for } U_{cell} > U_{TB} \quad (13b)$$

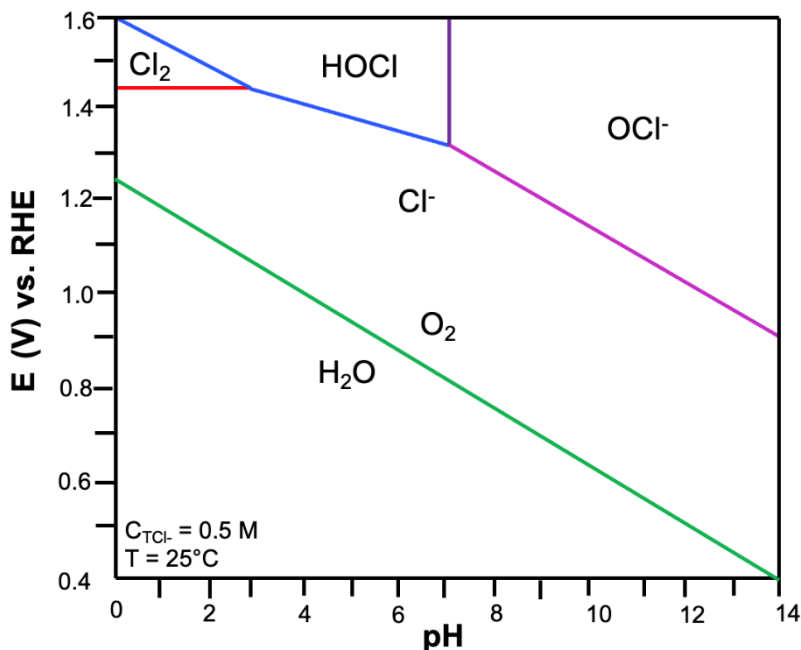
21 To conclude, the decreases of the vapor pressure ( $p_w$ ) and the specific conductance of  
 22 the electrolyte with the use of seawater will increase the reversible voltage ( $U_{rev,T,p}$ ), the  
 23 thermobalanced voltage ( $U_{TB}$ ), and the applied cell voltage ( $U_{cell}$ ) decreasing the  
 24 efficiency.

## 25 **III. Critical Challenges at the Anode**

26 The strategic exigency for a design at the anode that mitigates the chemical and  
 27 mechanical degradation of the overall electrolyser performance during seawater  
 28 electrolysis is convoluted in part by the chlorine species that can form upon perturbing  
 29 the solution pH and adjusting the potential applied at the anode.

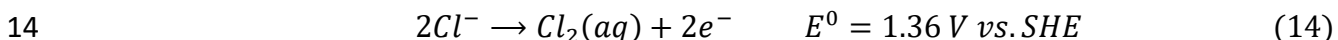
### 30 **III.1 Thermodynamic Constraints of the OER and CER**

1 The reduction-oxidation equilibria of the predominate chloride species at certain pH and  
 2 electrical potential is given by the Pourbaix diagram in Fig. 6 [20,72,73].



3  
 4 Fig. 6. Pourbaix diagram of a salinated aqueous electrolyte (0.5 M NaCl) indicating the stable chemical species that  
 5 are evolved as the pH and electrode potential are varied. The green line represents the pH and electrode potential  
 6 values at which a thermodynamic equilibrium between water and oxygen exists; pH and electrode potential  
 7 combinations above this line indicate regions at which oxygen can be evolved from water. The red line similarly indicates  
 8 the electrode potentials and pH values where chlorine gas is evolved. The blue line and the magenta line indicate  
 9 the onset of the hypochlorous acid and hypochlorite ion, respectively. The purple line indicates the pH and electrode  
 10 potentials at which a thermodynamic equilibrium exists between the hypochlorous acid and hypochlorite.

11 Different chemical species can be electrochemically generated from the parasitic  
 12 oxidations of the chloride ion including Cl<sub>2</sub>, HClO, and ClO<sup>-</sup> in acidic, neutral, and basic  
 13 pH conditions. Specifically, under acidic conditions,



15 Moreover, it is apparent that the voltage difference between the OER and the  
 16 thermodynamically unpreferred formation of hypochlorite is largest under basic conditions  
 17 (480 mV). This difference promotes the high OER selectivity evident in alkaline seawater  
 18 electrolysis [72]. Non-PGM catalysts stable in these basic conditions have been reported  
 19 with OER faradic efficiencies approaching 100 % [72,74,75].

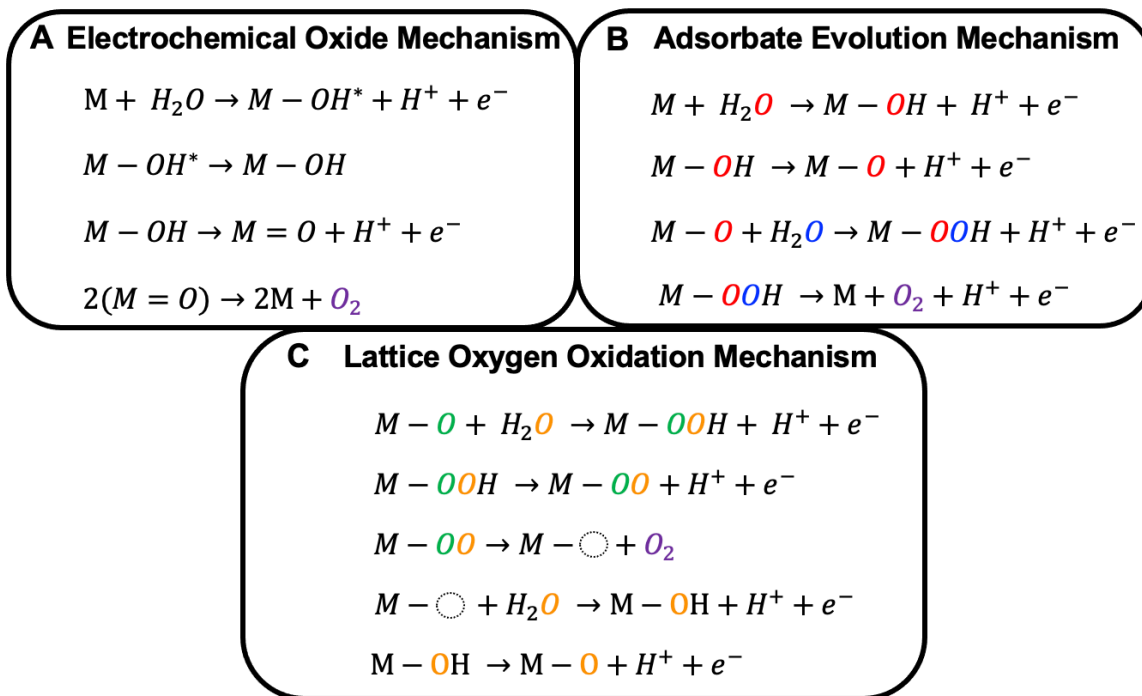
### 20 III.2 Heterogeneous Mechanisms of the OER and the CER

21 Present in a phase different from the reactants, heterogenous catalysts are easily  
 22 separable from the reactants and the products after the reaction. Thus they are very  
 23 desirable for high volume transformations such as those within the energy sector. The  
 24 heterogeneous catalysts interact strongly with the reactants, intermediates, and products  
 25 in what is known as an inner sphere electrode reaction, or the electron transfer can occur  
 26 through a monolayer of solvent in between the solid catalyst and the reactants, products,  
 27 and intermediates in what is known as an outer sphere electrode reaction [76]. Indeed,  
 28 the characteristics of the interface can greatly influence the rate of electron transfer, the



1 required overpotential, and the resulting faradaic current. Three different major  
 2 mechanisms are referenced in the literature for the OER: the electrochemical oxide  
 3 mechanism (EOM), the adsorbate evolution mechanism (AEM), and the lattice oxygen  
 4 oxidation mechanism (LOM).

### 5 III.2.1 Elucidated Mechanisms for the Oxygen Evolution Reaction



6  
 7 Fig. 7. Proposed reaction pathways for the oxygen evolution reaction elucidated (a) from Tafel kinetics and DFT  
 8 studies, (b) through DFT studies, and (c) by a combination of DFT, OLEMS, XPS, and XAS.

#### 9 III.2.1.1 Electrochemical Oxide Mechanism.

10 Initial evidence demonstrating the effect that the solid electrocatalyst can have on the  
 11 kinetic rate of the reaction was first mounted by Bockris et al., who found the rate of  
 12 electron transfer to be dependent on the work function of the metal [77,78]. J. O'M.  
 13 Bockris was also the first to calculate the corresponding Tafel slope for different  
 14 considered reaction mechanisms in the oxygen evolution reaction. The approach  
 15 assumed only one step in the mechanism was rate determining. Thus, the produced  
 16 intermediates from the non-rate determining steps were present in only small  
 17 concentrations and the saturation of the surface was only appreciable with the reactants  
 18 of the rate determining step [79]. These calculations were compared to Tafel slopes  
 19 obtained from experimental analysis of the log current vs. overpotential data and an  
 20 electrochemical oxide path was proposed. The EOM was later refined by Over and  
 21 Castelli et al. with DFT calculations. They propose an additional structural rearrangement  
 22 of the bound oxide (step 2) to be the rate determining step as shown in Fig. 7a [80,81,82].  
 23 By further studying the relative stabilities of the most pertinent spin states through DFT,  
 24 Busch et al. modeled the OER reaction cycle of a biomimetic catalyst, a  $\mu$ -OH Mn(III-V)  
 25 dimer bridged through hydroxide entities and truncated with acetylacetonate-type ligands  
 26 [83]. The electrochemical oxide mechanism was confirmed with an oxidation of Mn-OH

1 to Mn=O prior to the generation of O<sub>2</sub>, which was found to occur through a chemical step  
2 in which the two Mn=O moieties recombine in what has become known as a binuclear  
3 mechanism [83,84].

#### 4 *III.2.1.2 Adsorbate Evolution Mechanism.*

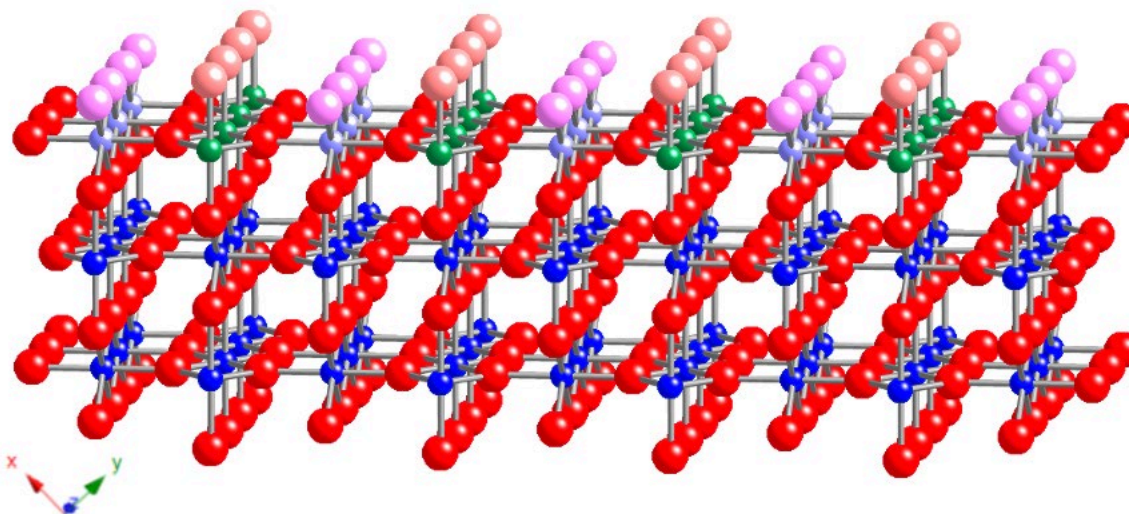
5 The proposed proton concerted electron transfer (PCET) mechanism shown in Fig. 7b,  
6 known as both the adsorbate evolving mechanism and the mononuclear mechanism, is  
7 thought to initiate with an acid-base nucleophilic attack [85,86].

8 To theoretically study this mechanism, the ( $\Delta G_{RX}$ ) of each intermediate formed in the  
9 pathway has to be computed. It requires the computing of the chemisorption ( $\Delta\epsilon$ ), the  
10 zero-point energy adjustment ( $\Delta ZPE$ ), and the entropy ( $\Delta S$ ) as shown in Eq. (15), though  
11 also corrected for the total energy of the gases [87,88],

$$12 \quad \Delta G_{RX} = \Delta\epsilon(z) + \Delta ZPE - T\Delta S \quad (15)$$

13 The chemisorption energy is quantified by measuring the change in potential energy of  
14 the adsorbate-catalyst system ( $\Delta\epsilon_{pot}$ ) as a function of the adsorbate distance ( $Z$ ) above  
15 the solid surface [89]. To calculate ( $\Delta\epsilon$ ), Norskov et. al. developed the computational  
16 hydrogen electrode (CHE) method. Rather than computing the solvation energies of the  
17 electrons and protons, Norskov et. al. assumed a chemical equilibrium between gaseous  
18 hydrogen molecules and solvated protons and electrons [90]. Thus, a simple computation  
19 of the free energy of the H<sub>2</sub> molecule in the gas phase can be conducted and the free  
20 energy ( $\Delta G_{RX}$ ) of each intermediate reaction (i.e.  $M - OH \rightarrow M - O + H^+ + e^-$ ) can be  
21 calculated as the free energy of the reaction  $M - OH \rightarrow M - O + \frac{1}{2}H_2(g)$ .

22 One example of the calculated chemisorption energies ( $\Delta\epsilon$ ) of each intermediate onto  
23 active surface sites was made by Rossmeisl et. al. on a (110) RuO<sub>2</sub> surface [91]. The  
24 active surface sites consisted of either a bridge site between two fourfold coordinated  
25 metal ions (in purple), or a coordinately unsaturated site (CUS) located on top of a fivefold  
26 coordinated metal at the surface (in light orange) in Fig. 8.



1  
2 Fig. 8. Representation of the bulk Ru and O atoms in blue and red, respectively, and the surface atoms, consisting of  
3 bridging Ru sites in purple and CUS Ru sites in green. Oxygen adsorbates on the electrochemically active Ru CUS  
4 sites are shown in light orange and the pink atoms on the Ru bridge sites represent surface oxygens.

5  
6 The mononuclear mechanism considers the CUS sites to be the primary active site on  
7 the surface of the rutile metal oxide structure [92]. The activation of bridge sites, that can  
8 occur by doping the metal oxide, creates a proton donor-acceptor moiety. This  
9 modification can initiate the bifunctional OER mechanism [92] and the bifunctional OER  
10 mechanism 2. These mechanisms differ only in that the splitting of the water during the  
11 formation of the peroxide adsorbate occurs electrochemically in the first and chemically  
12 in the second [93,94].

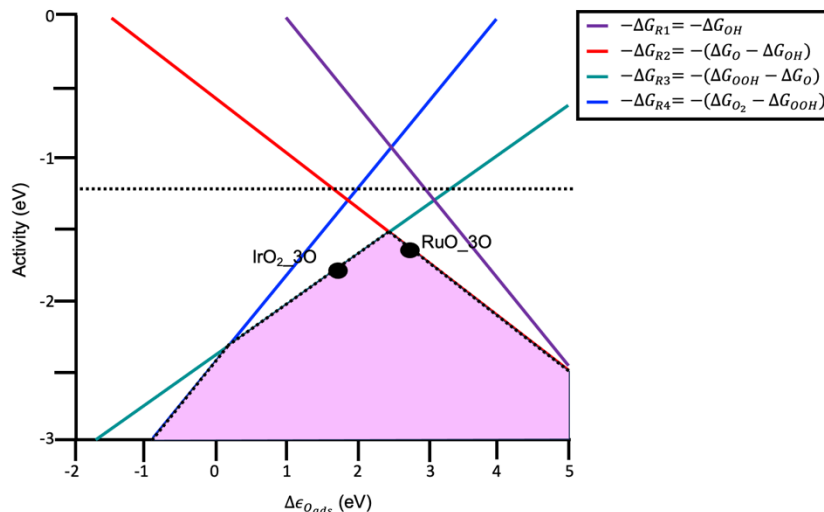
13 The chemisorption energies of these intermediates can be utilized to calculate the Gibbs  
14 Free Energy ( $\Delta G_{RX}(U)$ ) of each reaction step (X) in the mechanism as a function of the  
15 electrode potential ( $U$ ) [91].

$$16 \quad \Delta G_{RX}(U) = \Delta G_{RX} - ne_0U + k_bT pH \ln 10 \quad (16)$$

17 The potential determining step is the formation of the intermediate peroxide. Assuming  
18 that the rate determining step is determining by the potential determining step, the  
19 reaction mechanism may be deduced on a thermodynamic basis  
20 [[95], [96], [97], [98], [99]]. To minimize the overpotential required to complete the  
21 reaction, the energies of the three intermediates must be tuned. However, Rossmeisl and  
22 coworkers further found that the energies of the different intermediates are linearly  
23 correlated and are thus unable to be varied independently. It further limited the ability to  
24 optimize the electrocatalyst towards catalyzing the reaction at the minimum reversible  
25 potential value ( $E_E$ ) of the overall reaction [95,96,100].

26 Thus computing the chemisorption energy of the second intermediate of the pathway  
27 depicted in Fig. 7.b ( $M - O_{ads}$ ) enables the  $\Delta G_{RX}$  value for the  $M - OH_{ads}$  and  $M - OOH_{ads}$   
28 intermediates to be determined. Indeed, this constant difference of 3.2 eV between the  
29  $\Delta G(M - OH_{ads})$  and  $\Delta G(M - OOH_{ads})$  rather than the ideal 2.46 eV indicates an inherent  
30 overpotential [101]. Further optimizing the proton donor/acceptor functionality of the  
31 bridge sites along the ruthenia catalyst surface and activating the bifunctional

1 mechanisms has been proposed to break that scaling relation [92]. Finally, by modeling  
 2 ( $\Delta\epsilon$ ), the ability of the catalytic surface to form the chemical bond with the  $M - O_{ads}$   
 3 intermediate, the reaction rate, the catalytic activity, of electrocatalyst for the OER can be  
 4 calculated [102]. By thus plotting the catalytic activity as a function of the  $\Delta\epsilon_{M-O_{ads}}$ , a  
 5 volcano-shaped curve can be obtained, as shown in Fig. 9.



6  
 7 Fig. 9. The theoretical activity of the four charge transfer steps of the proposed AEM oxygen evolution reaction on a  
 8 metal oxide surface. Along the y axis are the activities of each step along the proposed reaction pathway, which are  
 9 shown to be linearly coordinated with the oxygen dissociative chemisorption energies plotted on the x axis along the  
 10 oxide surface. The resulting volcano curve is highlighted in pink and outlined in dotted lines with the position of two  
 11 potent catalysts, iridium dioxide and ruthenium dioxide with saturated bridge sites and vacancies at the CUS sites. The  
 12 best possible catalyst would catalyze the reaction at the horizontal dotted line indicating the equilibrium potential of  
 13 1.23 eV. Figure adapted from Rossmeisl et al. [103].

14 The apex of the volcano plot, known as the Sabatier maximum, is defined at the oxygen  
 15 interaction energy at which the oxygen coverage is constant and the formation of the  
 16 ( $M - OOH_{ads}$ ) peroxide intermediate becomes possible [91]. This maximum illustrates  
 17 the Sabatier principle, which states that the reaction rate is maximum at an optimum  
 18 interaction strength of the adsorbates with the catalyst. A stronger interaction inhibits the  
 19 release of the  $O_2$  molecules and poisons the surface and a too weak interaction is  
 20 indicative of an incomplete surface site coverage of the  $M - O_{ads}$  and an inability to  
 21 promote the formation of the peroxide intermediate [104].

22 This Sabatier maximum of Fig. 9 has a characteristic activity along the y axis smaller than  
 23 the ideal equilibrium value of 1.23 eV (horizontal dashed line). In the AEM, there is an  
 24 inherent thermodynamic impediment to the maximum activity of a catalyst coming from  
 25 the observed linear scaling relationship previously discussed. Indeed, the competition  
 26 between the  $-OH$  bond cleavage (step 2, Fig. 7b) and the formation of the ( $M - OOH_{ads}$ )  
 27 peroxide intermediate renders a minimum theoretical overpotential of 0.4 eV. Thus  
 28 catalyzing the mechanism with an applied potential of just 1.23 V when the system is at  
 29 equilibrium is considered thermodynamically unrealizable [96]. Additional energy, or  
 30 driving force, is required to promote the rate and observed current of the water splitting  
 31 reaction in the direction of oxygen evolution.

32 Lastly, it was shown that the mechanism at the apex of the volcano plot is highly  
 33 dependent on the applied potential [93]. By applying an overpotential of 200 to 400 mV,

1 Exner demonstrated the prominence of a Walden inversion mechanism, similar to the  
2 AEM with the concurrent formation of gaseous oxygen and adsorption of a water molecule  
3 in the final step of the pathway [105]. It worth noting that this inversion contributes to the  
4 degradation of rutile  $\text{RuO}_2$  electrodes [106]. Binninger further found that at applied  
5 potentials close to the equilibrium potential, crystalline  $\text{IrO}_2$  (110) preferentially catalyzes  
6 the OER through the availability of an  $\text{Ir}^*\text{OO}$  surface entity. The active sites were found to  
7 be the oxygen atoms at the crystalline  $\text{IrO}_2$  (110) surface, avoiding Ir–O bond breaking  
8 and justifying the evidenced stability of crystalline  $\text{IrO}_2$  towards the OER [107]. The  
9 applied potential was further shown to affect the electrocatalytically produced current  
10 through the amount of oxidative (rather than capacitive) charge accumulated within the  
11 catalyst. This indicate a decrease in the activation free energy of the rate determining  
12 step with the amount of charge stored [108].

### 13 *III.2.1.2.1 Descriptor Development.*

14 The slope of the volcano curve, which assumes a single elementary reaction governs the  
15 rate of the reaction, has been shown to change both at the legs and at the apex of the  
16 curve as the preferred mechanism adjusts or another elementary step begins to dictate  
17 the rate [109]. These phenomena add complexity of predicting selective catalysts for the  
18 OER and CER. Adequate descriptors, such as the energetic span [110] and the  
19 electrochemical step symmetry index [111] have been developed. Utilizing heuristic tools  
20 which incorporate the overpotential into the volcano-based analysis allow to assess the  
21 performance of electrode compositions [[109 ],[112], [113], [114], [115]]. As previously  
22 shown, the volcano curve is resolved from calculations of the potential determining steps,  
23 which may indeed differ from the rate determining step. Exner determined that for small  
24 overpotentials the potential determining step may differ from the rate determining step  
25 and only approach the rate determining step at large overpotentials [21,112]. The  
26 descriptor  $G_{max}(\eta)$  was proposed to replace the thermodynamic overpotential ( $\eta$ ) and the  
27 use of the potential determining step as a classification for catalytic activity as it can  
28 approach the rate determining step for typical reaction conditions. The use of  $G_{max}(\eta)$  can  
29 elucidate the chemical steps of a reaction pathway and can be coupled with a microkinetic  
30 approach to approximate current densities. It can resolve discrepancies in the rate  
31 determining steps of a reaction pathway with a predetermined Tafel slope [116].  
32 Furthermore, it was shown to be an effective approach towards predicting the selectivity  
33 between the OER and peroxide formation as the effect of the applied overpotential on the  
34 surface coverage could be accounted for and an evaluation of the evolved current  
35 densities could be made [116,117].

36 Many other OER activity descriptors such as the  $e_g$  orbital filling of transition metal ions  
37 [118], the shifting of the redox potentials through the inductive effect of foreign metal  
38 substitution [119], the covalence of the oxygen-metal bonds [120], and structural factors  
39 such as the lattice spacing of the metal electrodes [121], the M–O–M bond angle and the  
40 ability of the crystal structure to accommodate the ion size (Goldschmidt tolerance factor)  
41 have been proposed [122]. Though if in-situ surface reconstruction induced by the OER  
42 is indeed appreciable including loss of the crystal matrix and variable densities of the  
43 electrocatalytic active sites, the utility of these descriptors may be limited [121,123].

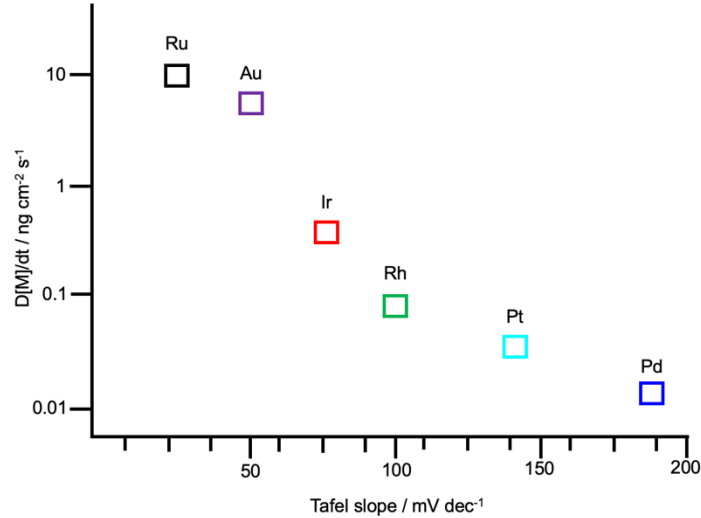
### 44 *III.2.1.3 Lattice Oxygen Oxidation Mechanism.*

1 The lattice oxygen oxidation pathway depicted in Fig. 7c, is similar to a Mars-Van  
2 Krevelen mechanism. It has the potential to surpass the inherent limitation (scaling  
3 relationship) of the AEM by the lattice oxygen participation through direct O–O coupling  
4 in the oxygen evolution pathways. Therefore, the inevitable catalyst instability must be  
5 addressed [124,125].

6 Initial observation of the drastic surface reconstruction that occurs in many OER catalysts  
7 led Grimaud et al. to study the influence of the substitution of a monovalent alkaline metal  
8 in  $\text{La}_2\text{LiIrO}_6$  perovskite. By doing this, higher Ir oxidation states are stabilized and they  
9 can prove unambiguously that the metallic  $t_{2g}$ -like  $\pi^*$  states are inactive for the OER  
10 [126]. Instead, the active surface sites on highly oxidized Ir-based catalysts are shown to  
11 be the lattice surface oxygen species that become more electrophilic upon oxidation. The  
12 computation of the Fukui function to render electron density maps indicated the  
13 participation of non-bonding oxygen states at the Fermi level upon Li removal and Ir  
14 oxidation, creating electrophilic oxygen radicals susceptible to nucleophilic attack by  
15 water oxygen lone pairs [126]. Grimaud et al. combined online electrochemical mass  
16 spectroscopy (OLEMS) and DFT calculations to reveal that the  $\text{O}_2$  generated by catalytic  
17 oxides with high activity towards the OER can derive from the oxygens within the lattice  
18 [120,125,127]. Furthermore, these oxides exhibited pH dependent OER activity which  
19 indicated that the proton transfers in the OER mechanism (step 2) are nonconcerted  
20 [120,125]. This pH dependency provides a lever to increase the efficiency of water  
21 electrolysis in the electrolyzers. Saveleva et al. furthermore confirmed that the generation  
22 of the electrophilic oxygen anion reactive intermediate can occur on both electrochemical  
23 iridium oxides (hydrated and amorphous) and thermally generated iridium oxides (of the  
24 crystalline rutile structure) through DFT analysis and operando studies using soft X-ray  
25 absorption spectroscopy at the O-K edge and near atmospheric pressure-XPS at the core  
26 levels of Ir 4f and O 1s [128].

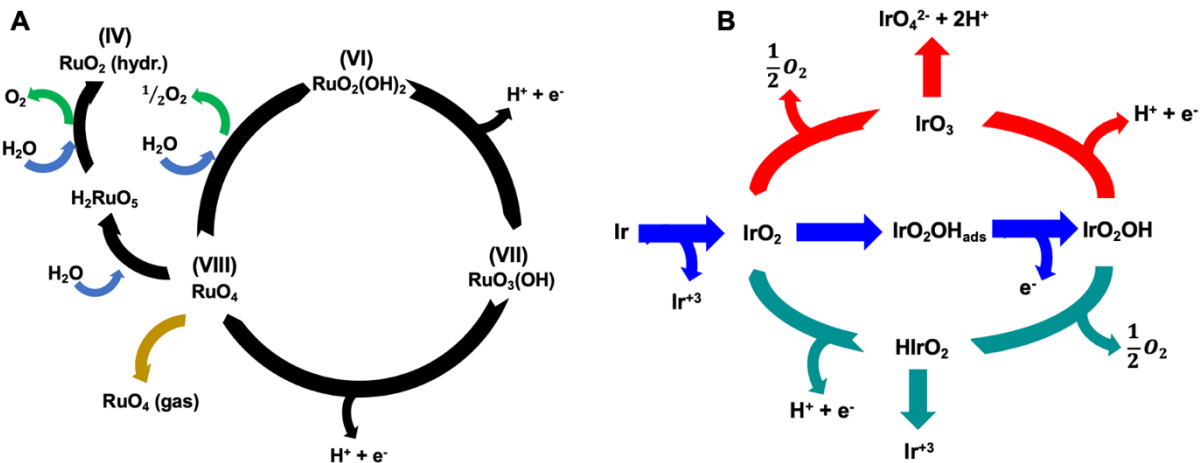
### 27 III.2.2. Stability Predicament at the Anode

28 The LOM may affect the stability of the material and enhance its susceptibility towards  
29 degradation. Indeed, disruption of the catalytic surface was evidenced to promote  
30 dissolution. Cherevko et al. found Ru to have the highest rate of dissolution among six  
31 different noble metals including Ir indicated for acidic water electrolysis as shown in Fig.  
32 10 [129].



1  
2 Fig. 10. A scatter plot of the dissolution rate at  $j = 5 \text{ mA cm}^{-2}$  determined through scanning flow cell/inductively coupled  
3 plasma mass spectrometry as a function of the Tafel slope taken from ohmic drop compensate current-potential curves  
4 scanned at  $2 \text{ mV s}^{-1}$ . Reproduced from Cherevko et al. [129].

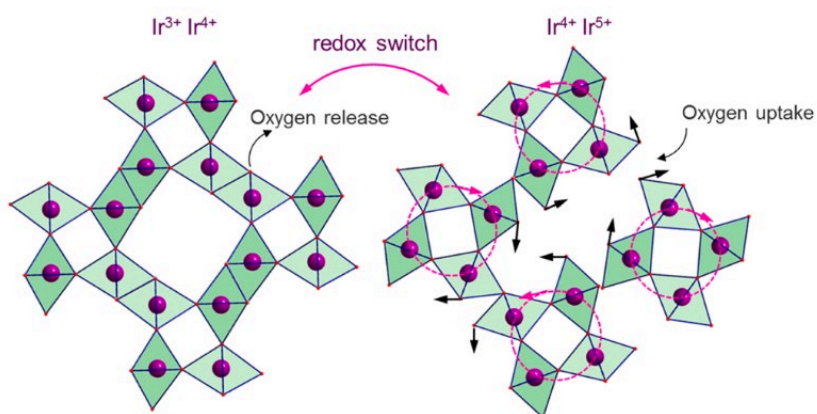
5 Shown in their respective Pourbaix diagrams, both the Ir and Ru metals become  
6 passivated at pH = 0 at a voltage of  $\sim 0.9 \text{ V}$ . The  $\text{IrO}_2$  oxide layer is further indicated to be  
7 stable up to a potential of  $2 \text{ V}$  under acidic conditions, whereas  $\text{RuO}_2$  begins to  
8 electrochemically dissolve to volatile  $\text{RuO}_4$  under acidic conditions at a mere  $1.4 \text{ V}$  [130].  
9 More specifically, the intermediate specie Ru (IV) is proposed to be the substrate for  
10 oxygen evolution and corrosion reactions [131]. Both of these processes were determined  
11 by Kötzt et al. to proceed towards Ru (VIII) through two single-electron transfer steps as  
12 shown in Fig. 11a, with the relative stability of Ru(VI) determining whether the Ru (VIII)  
13 corrodes or volatilizes, or dissociates to Ru (VI) [131]. Kasian et al. found the dissolution  
14 products of  $\text{IrO}_2$  to be potential dependent as shown in Fig. 11b with the formation of Ir(V)  
15 occurring regardless of the starting electrode material and the potential [132].



16  
17 Fig. 11. (A) Depiction of the Ru metal oxidation state during the oxygen evolution and corrosion processes on Ru and  
18  $\text{RuO}_2$  electrodes reproduced from Kötzt et al. [131] (B) Ir dissolution scheme at higher anode potentials indicated in red

1 arrows, at lower anode potentials indicated in green arrows. The blue arrows indicate the pathway of dissolution  
 2 intermediates that occur irrespective of the potential and electrode material. Figure adapted from Kasian et al. [132].

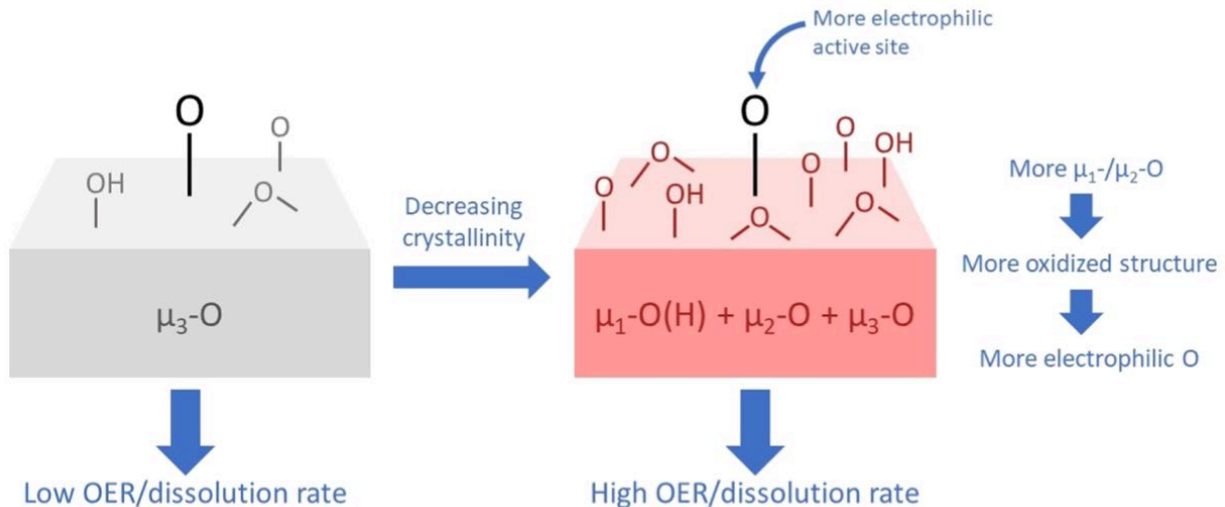
3 Ir and Pt were found to have lower steady-state dissolution rates [129]. Their however  
 4 higher rate of transient dissolution was proposed to be caused by the higher kinetic rate  
 5 of initial iridium oxide formation. Furthermore, amorphous iridium oxides were shown to  
 6 be more sensitive to transient dissolution processes though also showed a superior  
 7 activity towards the OER [133,134]. This high recorded activity is thought to be  
 8 independent of the increase in surface area. Evidence shown by Schweiner et.al. of O  
 9 atom exchange between the oxide lattice and water of up to 2.5 nm below the catalytic  
 10 surface suggests that all the atoms in these smaller particles sizes can be enabled  
 11 [135,136]. Indeed, Willinger et.al found IrO<sub>x</sub> samples with high electrochemical activity  
 12 towards the OER to consist of a hollandite-like structural motif with a IrO<sub>6</sub> structural  
 13 distortion creating a ratio between corner- and edge- sharing units; mixed Ir-oxidation  
 14 states were moreover found [137]. This open three-dimensional network of short range  
 15 order is proposed to encourage a redox mechanism that enables the uptake and release  
 16 of oxygen atoms through the rotating corner-sharing and edge-sharing units, uninhibited  
 17 by concerted motions that would be required of long-range ordered structures as shown  
 18 in Fig. 12 [137].



19  
 20 Fig. 12. Proposed redox mechanism of hollandite-like structural motifs of amorphous iridium oxides.

21 Mom et al. further found that amorphous iridium oxides contained more CUS sites and O-  
 22 bridge sites than crystalline rutile type IrO<sub>2</sub> that can be deprotonated upon the application  
 23 of a potential [133]. This deprotonation increases the electrophilicity of the active sites  
 24 and decreases the activation barrier for O–O coupling as indicated in Fig. 13. Thus, a  
 25 higher density of CUS and bridge sites in amorphous iridium oxides increase the  
 26 electrochemical activity [133]. However, this activity was simultaneously shown to lower  
 27 the barrier for Ir dissolution [133]. Thus strategies centered on the design of amorphous  
 28 iridium oxide anodes may aid in improved selectivity between the OER and CER;  
 29 however, the stability of the electrode may still be questionable.



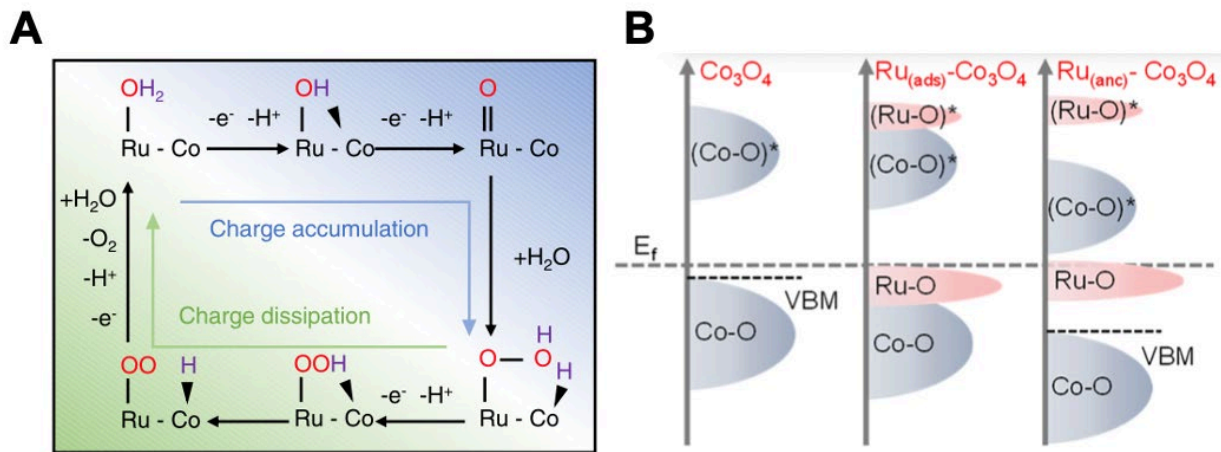


1  
2 Fig. 13. Representative depiction of the adverse effect of decreasing the crystallinity of iridium oxide. Amorphous iridium  
3 oxides were shown to consist of more CUS sites ( $\mu_1$ ) and bridge sites ( $\mu_2$ ) in addition to bulk oxygen sites ( $\mu_3$ ) that  
4 were susceptible to deprotonation under anodic potentials, creating electrophilic oxygen atoms on the electrode surface  
5 that lowered the rate-limiting barrier for O-O coupling. Figure of Mom et al. [133].

6 Interestingly, Willinger et al. had found that the residual K ions localized in the large  
7 tunnels of the hollandite-like open structure of amorphous  $\text{IrO}_x$  could stabilize the catalyst  
8 [137]. Thus, Xu. et al. prepared an  $\text{IrO}_x$  catalyst with incorporated hydronium ions through  
9 rapid oxidation of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  in molten salts. It achieved negligible degradation after 8  
10 months of hydrogen production in a three-electrode cell test in 0.1 M  $\text{HClO}_4$  [138]. OLEMS  
11 with isotopic labeling further indicated that the lattice water accommodates into the  
12  $\text{IrO}_x$  framework as hydronium ions that undergo nucleophilic attack by the water adsorbed  
13 on the electrocatalytic surface at anodic potentials, initiating a modified AEM mechanism  
14 [138].

15 Encouraging the AEM mechanism for OER electrocatalysis may indeed improve the  
16 stabilities of the materials. Lu et al. found that the OER mechanism could be switched  
17 from AEM to LOM to AEM by manipulating the oxygen defect content of  $\text{La}_x\text{Sr}_{1-x}\text{CoO}_{3-\delta}$   
18 perovskites. They exhibit a volcano-type activity variation as the oxygen defect  
19 concentration increased [139]. The mechanistic manipulation and volcano activity  
20 variation was proposed to be caused by a concentration lockup of the generated  $\text{Co}^0$  with  
21 increasing O vacancies. DFT simulation found this lockup to be caused by a coupling  
22 between the p and d orbitals. This coupling induces interionic  $p\pi$  compensation, which  
23 can maintain the oxidation activities by the tailband of localized O-2p orbitals, and  
24 preserve the stability of the material through the transition back to the AEM mechanism  
25 [139]. A metal defect trapping technique was also utilized to synthesize Ru single atoms  
26 within the Co-O-Co skeleton of  $\text{Co}_3\text{O}_4$ . This configuration shifted the Co-O hybridized  
27 orbitals away from the Fermi level discouraging the removal of valence electrons and the  
28 activation of the lattice oxygen. In addition, the local geometry of the active centers was  
29 shifted from planar to a 3D local orientation. This change facilitates the proton transfer  
30 from the OER reaction intermediates to the bridging oxygen sites and broke the  
31 intermediate adsorption energy limitation as shown in the proposed mechanism of the  
32 study of Fig. 14 [140]. Thus, both the stability of the material was improved and an

1 overpotential of a mere 198.5 mV under acidic conditions was required to catalyze the  
 2 OER.

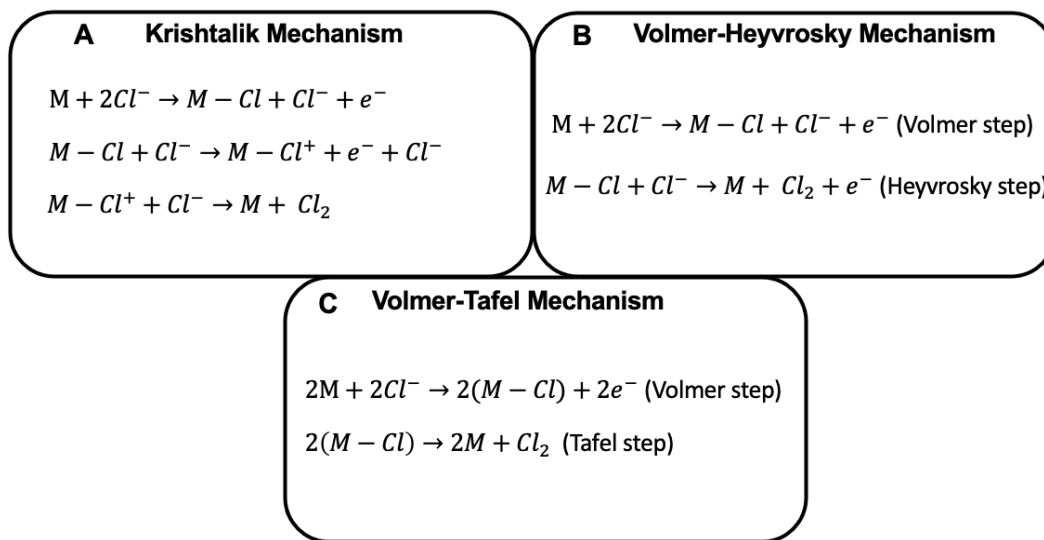


3  
 4 Fig. 14. (A) The proposed OER mechanism of an atomically dispersed Ru atom under a lattice-anchored ( $\text{Ru}_{\text{anc}}$ ) steric  
 5 configuration. (B) DFT calculations comparing the band centers of the  $\text{Ru-O-Co}$  system indicating downshifted  $\text{Co-O}$   
 6 hybridization in the  $\text{Ru}_{(\text{anc})}\text{-Co}_3\text{O}_4$  steric configuration, which decreased the tendency to lose valence electrons at  
 7 the Co sites and the participation of the lattice oxygen. Figure of Hao et al. [140].

### 8 III.2.3 Elucidated Mechanisms for the Chlorine Evolution Reaction

9 Understanding how the chlorine evolution reaction takes place was at first discussed  
 10 through calculations of indirect experimental Tafel slopes and reaction orders. Three main  
 11 mechanisms are reported in the literature. First, Krishtalik and Rotenberg initially deduced  
 12 the mechanism for chlorine evolution shown in Fig. 15a on graphite electrodes. They  
 13 proceed through the identification of a low Tafel slope on the anodic polarization curve  
 14 and a first order reaction with respect to the chloride ion that created a univalent positive  
 15 chlorine state. This result was later confirmed on  $\text{RuO}_2$  and  $\text{RuO}_2\text{-TiO}_2$  electrodes  
 16 [[141], [142], [143]]. Though Janssen and Hoogland argued that the electrode doesn't  
 17 behave as a porous material. Thus the electrochemical active surface area is nearly equal  
 18 to its external surface area, and found the chlorine evolution pathway to follow a Volmer-  
 19 Heyrovsky mechanism on a graphite anode. According to their analysis, the rate  
 20 determining step should be dependent on the degree of electrode aging [144]. Finally, Fita

1 et al. found evidence for the Volmer-Tafel mechanism of Fig. 15c on an electrode made  
 2 of a Pt-Ir alloy on a titanium substrate [145].



3  
 4 Figure 1: Classical chlorine evolution mechanisms derived by kinetic studies.

5 It was the discovery of the dimensionally stable anode (DSA), designed with a titanium  
 6 substrate and a mixed metal oxide composed of ruthenium dioxide and titanium dioxide,  
 7 that cut the energy consumed per ton of chlorine produced to nearly half [53]. Developed  
 8 initially by Beer, who patented the material in 1965, these DSA anodes replaced the  
 9 carbon electrodes, which are highly susceptible to corrosion under any crystalline  
 10 structure or morphology ( $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ ) [53,146,147]. Tethered with  
 11 more than 50 % of the entire global chemical production turnover, brine electrolysis  
 12 produces the globally demanded 90 million tons of chlorine and 100 million tons of sodium  
 13 hydroxide, positioning the industry as one of the largest chemical sectors, just behind  
 14 sulfuric acid and ethylene production [53]. As expected, the industry demands a large  
 15 consumption of electricity to power the voltage demands required to produce the current  
 16 densities for the evolution of chlorine at the anode and sodium hydroxide at the cathode.  
 17 These hydrophilic anodes designed by Beer could be engineered in the form of meshes  
 18 with a mud-cracking morphological pattern that enabled greater escape of gas bubbles,  
 19 decreasing the inner electrode gap and the gaseous oversaturation of the inner electrode  
 20 solution, reducing the ohmic drop [53,148]. Reducing the gas bubble size and the average  
 21 residence time at the electrode surface also promoted deblocking of the electrode active  
 22 sites; coverage of the active sites can increase the local overpotential and accelerate  
 23 corrosion [53,148]. Though the actual electrocatalytic properties of the material showed  
 24 only a modest improvement over the electrocatalytic properties of the carbon electrode  
 25 that was due to their powder-like consistency, which increased the surface area and  
 26 roughness factor [148]. It is the versatile nature of these highly conductive, active oxides  
 27 that promote their potentiality and robustness towards decreasing the activation energies  
 28 of critical electrochemical reactions [148].

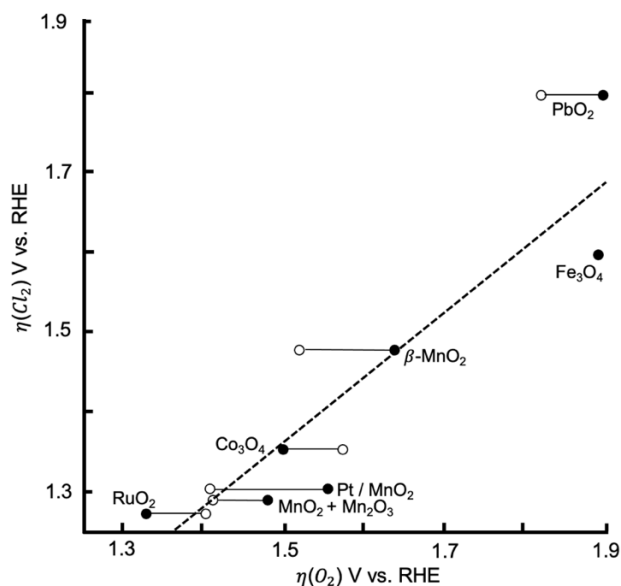
29 **IV. Facilitating the Electrocatalytic Performance at the Anode**

1 Enhancing the selectivity of seawater electrolysis with appreciable faradic efficiencies for  
2 oxygen and hydrogen evolution is convoluted by the multifarious complexity of the  
3 competition between CER and OER at the anode. Beginning to unravel that complexity  
4 enables strategies to be designed that break the scaling relationships select for the most  
5 active facet of the electrocatalyst, modulate the electrocatalytic surfaces with substitutions  
6 and vacancies, and augment the conductivity. Incorporating filtration approaches and  
7 taking inspiration from the observed self-healing properties of molecular electrocatalysts  
8 may lead to a heterogeneous electrocatalysts with a characteristic penchant for OER  
9 selectivity crucially needed to utilize the abundancy of seawater reserves to generate the  
10 hydrogen energy carrier.

#### 11 IV.1 OER vs. CER Mechanistic Competition

12 Usually in brine electrolysis, the oxygen evolution reaction is considered a parasitic side  
13 reaction hampering the selectivity for the chlorine evolution reaction at the DSA rutile-type  
14 anodes [149]. Under the aqueous NaCl or HCl conditions, the surface of the electrode  
15 can interact with water, chloride ions, or other ionic constituents of the electrolyte solution.  
16 Within the potential region of the chlorine evolution reaction that occurs beginning at 1.36  
17 V, there is a strong occurrence for the oxidation of water considering that the reversible  
18 voltage of water begins at 1.23 V. In further considering this contention by examining the  
19 adsorbate evolution mechanism for the OER, two electrons are transferred to form the  
20 adsorbed oxygen species whereas only one electron is transferred to form a chlorine  
21 intermediate. Thus the energy gained ( $= zeE$ ) for the adsorption of oxygen is double the  
22 energy gained for the adsorption of a chlorine intermediate. Therefore thermodynamics  
23 dictates that the electrode surface is effectively covered with the  $M - O_{ads}$  adsorbate  
24 under the potentials at which chlorine begins to evolve [150].

25 Trasatti conjectured that the chloride ion adsorbed onto the surface by binding the same  
26 single oxygen species ( $M - O_{ads}$ ). The slope of unity in the graph of Fig. 16 indicates that  
27 the AEM ( $-OH_{ads}$ ) adsorbate of the OER and the (-Cl) adsorbate of CER bind the catalytic  
28 surface through the same  $M - O_{ads}$  atom. Indeed each of these adsorbates adsorb onto  
29 the  $M - O_{ads}$  populating the surface with a one-to-one linear correlation [89,151]. Thus  
30 Trasatti observed that good oxygen evolving catalysts were also chlorine evolving  
31 catalysts. Trasatti also revealed that an additional overpotential is required for those  
32 catalysts to catalyze the oxygen evolution reaction [151]. This overpotential comparison  
33 indicates that the prevalent mechanism on these catalysts is indeed the AEM.

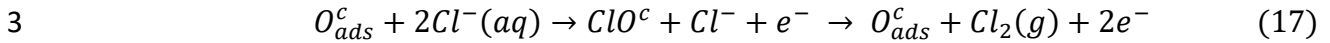


1  
2 Fig. 16. Plot of the overpotential for chlorine evolution against the overpotential for oxygen evolution recorded for  
3 various oxides at the same current density in acidic solution (•) and basic solutions (O). Figure adapted from Trasatti et  
4 al. [151].

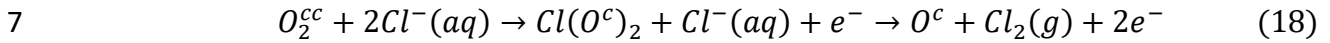
5 The initial density functional theory (DFT) studies to elucidate the potential, pH regions,  
6 chloride concentrations, and electrode materials in which this  $O_{ads}$  species was adsorbed  
7 on the electrode surface were conducted by Hansen et. al.. They analyzed the surface  
8 structure and the activity trends underlying the electrocatalysis of chlorine evolution over  
9 rutile oxides [152]. Further considerations for the effects of the solvent, the bridging lattice  
10 oxygen atoms, and the uncertainties of the DFT calculations were also studied [115, 153,  
11 154]. The unit cell surface consisted of two bridge sites ( $b$ ) and two CUS sites ( $c$ ) and the  
12 adsorbates were found to strongly bind the bridge sites. Thus the adsorbate binding  
13 stabilities at the CUS sites were probed. It was assumed that the activation energies ( $E_A$ )  
14 of the reactions were linearly correlated to the reaction chemisorption energies ( $\Delta\epsilon$ ) as  
15 previously described. It was found that adsorption of the CER adsorbates directly onto  
16 the CUS sites required a pH < -3 and formation of CER adsorbates directly on the bridge  
17 sites required an even lower pH [98, 152]. Plots of the  $Cl^c$  and  $ClO^c$  chemisorption  
18 energies against the  $O_{ads}^c$  chemisorption energies showed a similar trend seen in the plot  
19 of Fig. 16 and thus indicated that the chemisorption energies are linearly correlated. This  
20 phenomenon was thought to be caused by the identical valency of one found in both the  
21 chloride species and the oxygen atom of the hydroxide adsorbate precursor. Thus, a plot  
22 of the potential against the  $O_{ads}$  binding energy was generated and depicts the potential  
23 and  $O_{ads}$  chemisorption energy regions in which the most stable adsorbates can be found  
24 on the surface, as shown in Fig. 17. The three Sabatier volcano curves indicate chlorine  
25 evolution through the mechanistic pathway consisting of the  $ClO^c$ , the  $Cl(O^c)_2$ , or the  $Cl^c$   
26 intermediates. The blue line represents a combined Sabatier volcano that takes the  
27 stability of the initial adsorbate on the surface into account; the intermediate is only  
28 expected to form at active sites that are indeed stable and abundant.

29 The three metal oxides indicated in Fig. 17 each bind to the  $O_{ads}^c$  with a different  
30 binding energy and thus stabilize a different adsorbate and a different chlorine  
31 intermediate. Along the surface of  $IrO_2$ , the  $O_{ads}^c$  initiates the formation of the  $ClO^c$

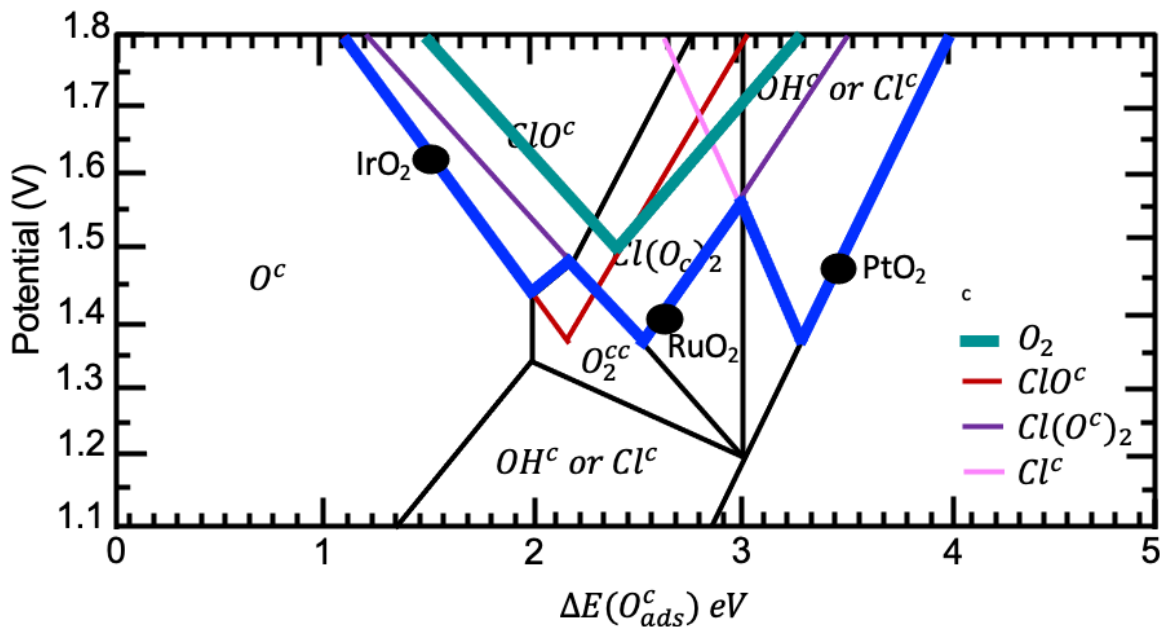
1 intermediate, which was further determined to follow a Volmer-Heyrovsky mechanism  
 2 [152,155,156].



4 Along the  $RuO_2(110)$  surface, the most stable adsorbate populating the CUS sites in the  
 5 potential regions of chlorine evolution is the  $O_2^{cc}$  adsorbate, enabling the formation of the  
 6 chlorine intermediate through the Krishtalik mechanism [152].



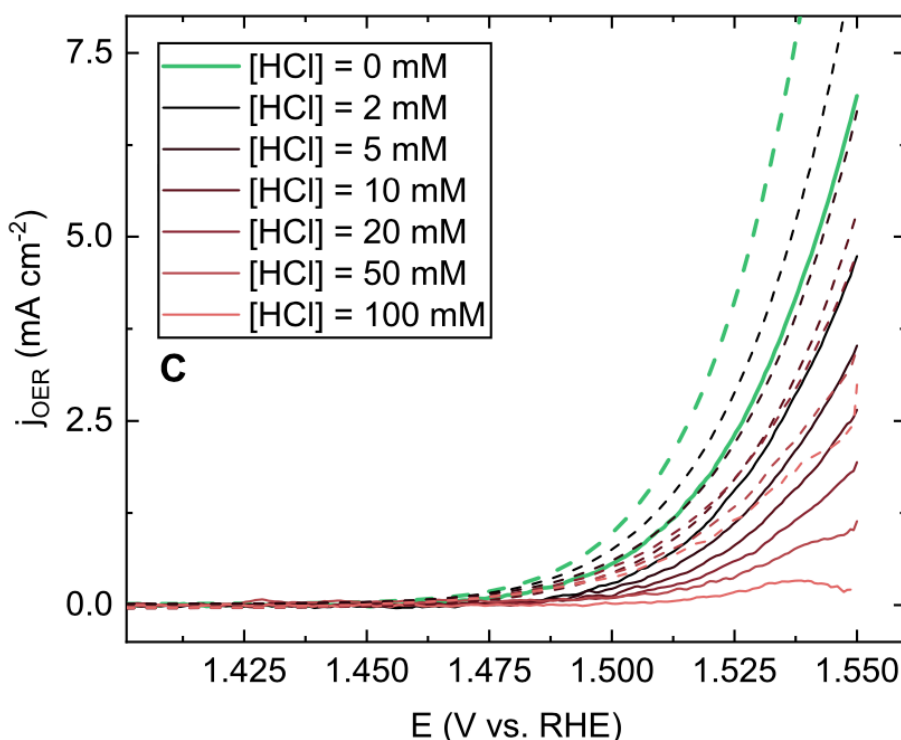
8 This analysis indicates that chlorine will evolve on  $IrO_2$  and  $RuO_2$  through the formed  $ClO^c$   
 9 and the  $Cl(O^c)_2$  intermediates at the CUS sites. Exner et. al. later proposed however that  
 10 the  $ClO^c$  adsorbate is also indeed the precursor for the CER on  $RuO_2(110)$  [153]. When  
 11 the combined Sabatier volcano curve for the chlorine evolution of Fig. 17 (*Blue Curve*) is  
 12 compared to the Sabatier volcano curve for oxygen evolution, as shown in Fig. 17 (*Green*  
 13 *Curve*), it is apparent that in accordance with the initial work by Trasatti, the CER will  
 14 evolve at lower potentials than the oxygen evolution reaction on oxides with characteristic  
 15 oxygen chemisorption energies. The CER occurs through a single intermediate, and thus  
 16 the mechanism isn't subjected to the linear scaling relationships between the three  
 17 intermediates inherent in the OER undergoing the AEM. Moreover, CER selectivity is  
 18 highly favored under conditions in which the  $Cl^c$  intermediate, rather than the  $ClO^c$   
 19 intermediate is formed at the rutile surface, even in only slightly acidic or even neutral pH  
 20 conditions [155].



21  
 22 Fig. 2: (Blue Curve) Combined Sabatier volcano curve that indicates the most stable adsorbate and formed intermediate  
 23 at a given  $O_{ads}$  binding energy and potential at pH = 0 and  $a_{Cl^-} = 1$ . (Green Curve) The Sabatier volcano for the OER  
 24 indicating that greater potentials are required to catalyze the reaction along  $IrO_2$ ,  $RuO_2$ , and  $PtO_2$ . Reproduced from  
 25 Hansen et al. [152].

26 IV.1.1 Confronting Competitive Adsorption

1 Vos et al. indicated that the OER reaction is suppressed in the presence of chloride ions  
2 through competitive adsorption and active site blocking [55]. Graphs in solutions showed  
3 decreasing OER activity as the concentration of the chloride ion (and the bromide ion)  
4 increased as shown in Fig. 18. The CER was further found to proceed through the Volmer-  
5 Heyrovsky mechanism, similar to the Rideal-Eley mechanism for gaseous reagents.



6  
7 Fig. 18. OER current density as a function of potential vs. RHE in the presence of bromide (solid curves) and without  
8 bromide (dashed curves) at increasing chloride ion concentrations. Figure of Vos. et al. [55].

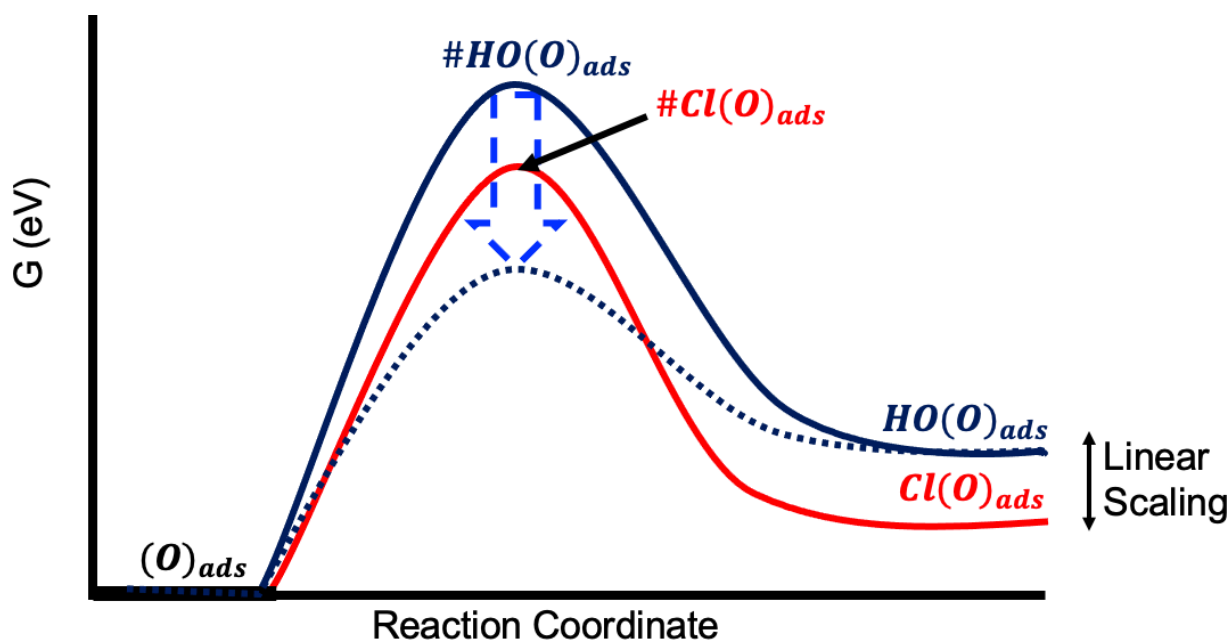
9 If a Langmuir adsorption model with a lack of lateral interactions among adsorption sites  
10 is assumed, the surface coverage of water at the active sites is thus expected to diminish  
11 in the presence of the chloride ion, though its presence at an approximately consistent  
12 concentration enables a small amount of oxygen to form, at the dismay of the chloro-alkali  
13 industry. Therefore, improving the selectivity at the anode is an inevitable challenge.

#### 14 IV.1.2 Identifying the Rate Determining Step

15 Efforts have been proposed to develop new electrocatalysts that maximize the free  
16 energy difference between the respective CER and OER intermediates. With the  
17 assumption of quasi-equilibrium of the reaction intermediates preceding the rate  
18 determining step in place, the free energies of the transition states corresponding to the  
19 rate determining step can be found, enabling the rate determining step to be identified  
20 [150,157]. With the desire to discover an electrocatalyst that stabilizes the oxygen  
21 transition state, the intrinsic catalytic characteristics of an electrocatalyst may be regarded  
22 through measurements of the exchange current density. Exner et.al. proposed that the  
23 linear regions of the Tafel plot may each be extrapolated to  $\eta = 0$  to measure the exchange  
24 current densities. They could then be utilized in the generalized Butler-Volmer equations  
25 discussed by Parsons to determine the free energy of the corresponding transition state,

1 enabling the rate determining step to be determined with respect to the overpotential  
2 applied [150,158].

3 The free energies of the reaction intermediates must be determined to enable a critical  
4 assessment of the intermediates and transitions states to stabilize and thus promote CER  
5 or OER selectivity. Quasi-equilibrium implies inaccessible values of reaction  
6 intermediates free energies. Though, advancement of transient experiments like cyclic  
7 voltammetry [159] and operando spectroscopic methods [160] can aid in their  
8 identification. However, with small surface area coverages due to their higher Gibbs Free  
9 energies, in-situ intermediate detection is generally difficult. A particular attention should  
10 be made to verify the reaction intermediates and their corresponding free energies  
11 determined through DFT theory and the construction of ab initio surface Pourbaix  
12 diagrams. The free energies in function of potential of reaction intermediates can be *ab*  
13 *initio* calculated and correlated with the respective free energies of their transition states  
14 determined through the Tafel plots. This work enables a free energy surface model of an  
15 electrocatalyzed reaction to be deduced and the dependence of the free energies of the  
16 transition states and reaction intermediates on the overpotential to be depicted.  
17 Understanding the characteristic rate determining step of a designed electrocatalyst with  
18 respect to the overpotential could enable optimization of an electrocatalyst that, for  
19 instance, stabilizes the ( $M - OO\text{H}_{ads}$ ) transition states, making the OER the kinetic  
20 product by increasing the speed of the reaction step as delineated in Fig. 19 [161].



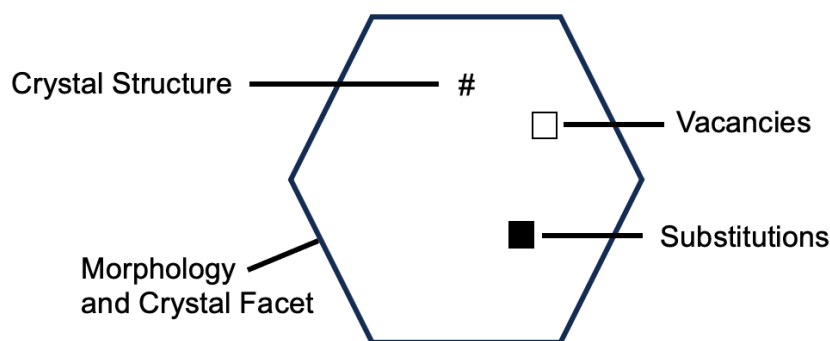
21  
22 Fig. 3: The free energy diagram along the reaction coordinate of the OER and the CER over a single-crystalline RuO<sub>2</sub>  
23 (110) electrode at  $\eta_{CER} > 0.1$  V and constant pH indicating the relative energies of the transition states (#) of the rate  
24 limiting steps for the OER and CER. The thermodynamic stabilities of the HO(O)<sub>abs</sub> and the Cl(O)<sub>abs</sub> intermediates are  
25 determined by the linear scaling relationships. Figure adapted from Exner [162].

## 26 IV.2. Modulating the Structure of the Electrocatalyst

27 Initial thoughts by Taylor implicated that unsaturation within an active site at the atomic  
28 level can control surface reactivity [163]. Refinement of the local structure can optimize  
29 the functionality of the active site. A challenge of heterogenous electrocatalysis is



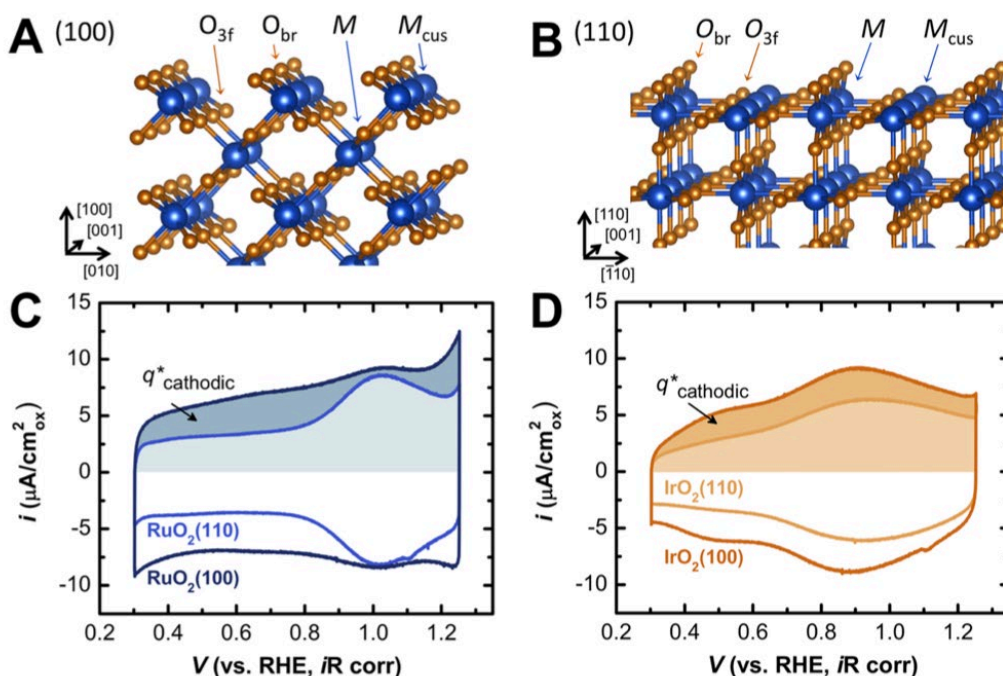
1 maximizing the exposed active sites and enhancing their intrinsic mass activity by  
2 stabilizing the transition state while maintaining stability. Refining the size and the  
3 dispersion, and moreover the crystal facet orientation, has been shown to improve the  
4 amount of exposed active sites [164]. Moreover, dispersing the active centers among  
5 various types of substrates such as metal oxides [165], metals sulfides [166], and carbons  
6 [167] can influence the ionic and electronic defects within the material and encourage  
7 electron transfer capabilities of the active centers, manipulating the valence of the active  
8 site and the coordinating bond lengths [168]. These refinements can influence the stability  
9 of the intermediates and the activation energies of the transition states electronically,  
10 geometrically, and through confinement effects enabling selective seawater electrolysis  
11 to be achieved [169,170] (Fig. 20).



12  
13 Fig. 20. Means of manipulating the active site to improve the activity and selectively of the electrocatalyst.

#### 14 IV.2.1. Manipulating the Morphology and Crystal Facet

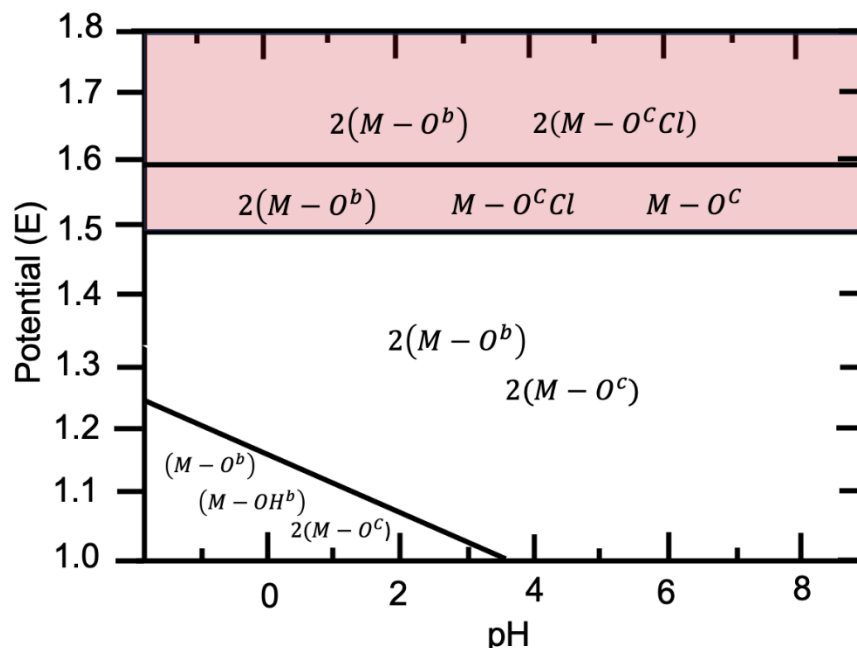
15 The D-band centers of late transition metals with low coordination numbers, consisting of  
16 edges, steps, and kinks are thought to be more diffuse, residing further from the nucleus  
17 and interacting more strongly with adsorbates than metal atoms on close packed surfaces  
18 with higher metal coordination numbers and more compact, tightly-bound d-states [169].  
19 Dickens and Norskov projected the density of states onto an Ru atom CUS-terminated  
20 single kink site along the (110) plane and found shifted d-band centers with significant  
21 higher energies, which result in less filling of the Ru–O adsorbate antibonding states and  
22 a stronger Ru–O adsorbate bond, promoting the OER [171]. Indeed, the structure of the  
23 catalytic surface has been shown to affect the catalytic activity of the material towards the  
24 OER through a linear correlation with the density of coordinatively undersaturated metal  
25 sites (CUS) along each crystallographic face [172]. The (100) facet of epitaxial grown  
26 RuO<sub>2</sub> supported on a single crystal (001) facet of SrTiO<sub>2</sub> was found to more easily oxidize  
27 the reagent substrate than the corresponding (110) facet in a basic 0.1 M KOH solution  
28 as shown in Fig. 21. Measurements of the cathodic pseudocapacitive charge further  
29 enabled a charge ratio between the two surfaces to be determined that was found to  
30 mimic the CUS ratio between the two facets [172].



1  
 2 Fig. 4: (A) Schematic depiction of the (100) facet and (B) the (110) facet of RuO<sub>2</sub> and IrO<sub>2</sub>. Fully coordinated metal  
 3 centers (M) and coordinately undersaturated metal sites (*M<sub>cus</sub>*) are indicated in blue, bridging oxygens (*O<sub>br</sub>*) and three-  
 4 fold coordinated oxygen (*O<sub>3f</sub>*) are shown in orange. Analysis of the pseudocapacitive charge (*q<sub>cathodic</sub>*<sup>\*</sup>) shown in (C)  
 5 and (D) for RuO<sub>2</sub> and IrO<sub>2</sub> gave an indication of the electrochemically active metal site density on the electrode surface,  
 6 the ratio of the calculated charge between each orientation indicating the undercoordinated metal site density. Figure  
 7 of Stoerzinger et al. [172].

8 The stepped nature of the (230) facet of RuO<sub>2</sub> was further proposed to explain the greater  
 9 Cl<sup>-</sup> evolution; the (230) facet possesses an activity with a greater susceptibility to changes  
 10 in the pH because of the abundant pre-oxidation occurring through proton removal of the  
 11 hydroxide adsorbates along the surface active sites [173,174]. This (230) surface was  
 12 indeed proposed to be more hydrophilic, possibly due to its unique binding energies with  
 13 the -H<sub>2</sub>O and -OH adsorbates, enabling different degrees of hydrogen bonding amongst  
 14 the adsorbate groups along the surface [175]. The mechanism of chlorine evolution was  
 15 further proposed to proceed without pre-oxidation on more hydrophobic surfaces such as  
 16 the (100) facet with less local functional group motion that facilitates proton exchange  
 17 [173]. Facilitating proton exchange may indeed be more facile on faceted surfaces. Adiga  
 18 et al. epitaxially grew a (101) surface of RuO<sub>2</sub> on r-Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> substrates, a surface  
 19 which is known to possess a large degree of strain due to the large lattice mismatch  
 20 between the film and the substrate [176]. This strain was shown to relax as the film  
 21 thickness increased through the introduction of facets and defect formation. This faceting  
 22 was shown to dramatically decrease the activity towards the OER, which was shown to  
 23 be perpetuated through the LOM evidenced by exposing the thicker films to solutions of  
 24 varying pH, the AEM mechanism is conjectured to independent of solution pH due to the  
 25 proposed concerted proton-electron transfers. Interestingly, the CER activity was  
 26 minimally affected. Strain relaxation and the resulting faceting may thus induce a  
 27 mechanistic change in the OER [176]. The study moreover found the thicker films to be  
 28 more selective for the CER.

1 Indeed, mitigating the elucidated mechanisms of the CER and the OER to select for one  
 2 evolved product is convoluted by the disparities between the single intermediate and the  
 3 multiple intermediate reactions. Interpretation of the most thermodynamically stable  
 4 intermediate, initially addressed by the DFT studies by Hansen et al. has aided in the  
 5 utilization of potential and pH manipulations to promote the evolution of the CER or the  
 6 OER [152]. Fig. 22 highlights the potential and pH conditions that promote the evolution  
 7 of the CER or the OER.



8  
 9 Fig. 22. Pourbaix diagram depicting the most stable adsorbates along the  $RuO_2(110)$  catalytic surface corrected for  
 10 solvent effects at Activity  $Cl^- = 1$ . Denoted adsorbate structures were further found to be stable with respect to the gas  
 11 phase molecular species. Potential and pH regions highlighted in red indicate the conditions promoting the CER; the  
 12  $2(M - O^b) + 2(M - O^c)$  structure is expected to serve as the catalytic active phase for the OER. Figure reproduced  
 13 from Exner et al. [153].

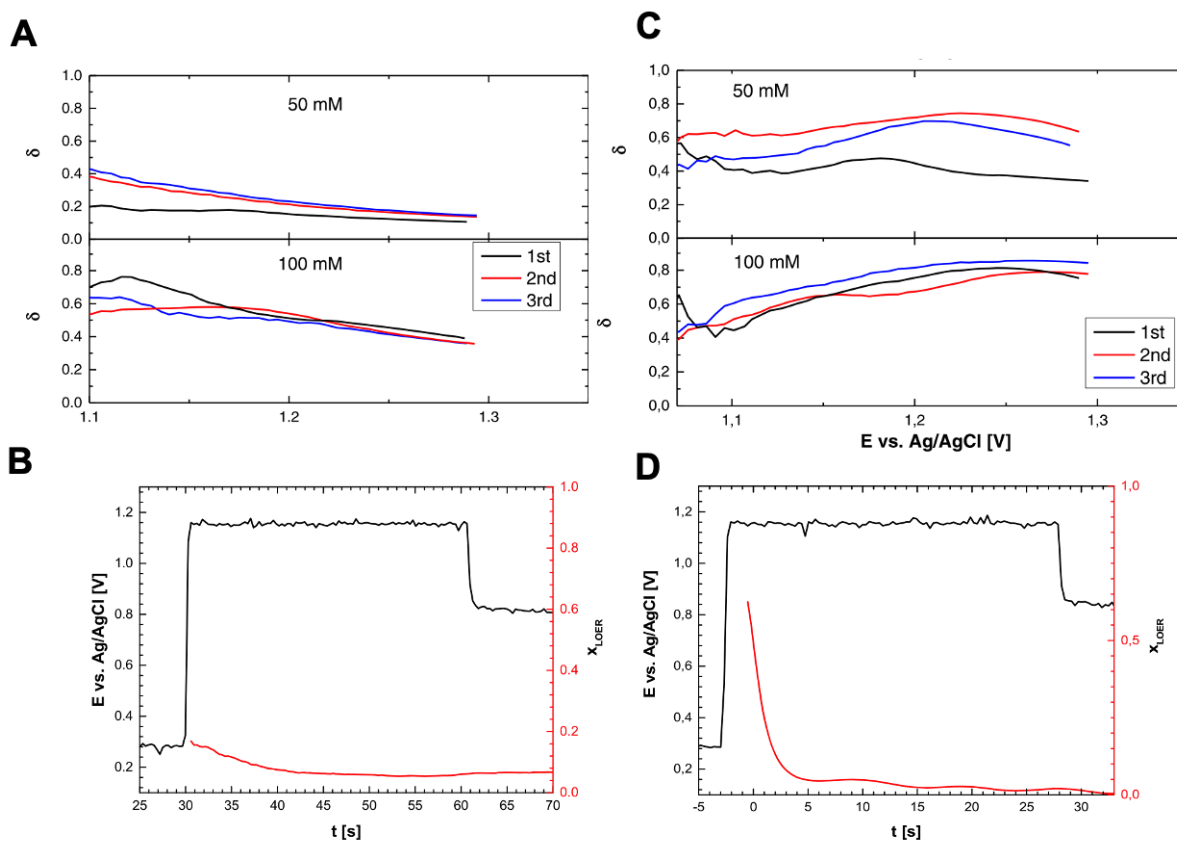
14 However, with the high current densities afforded by PEM electrolyzers, achieving OER  
 15 selectivity under acidic conditions is critical, requiring surface engineering that controls  
 16 the nature and abundance of the active sites that catalyze the desired reaction. Saha et  
 17 al. utilized ab-initio studies to further find the (101) and the (001) to be the most selective  
 18 facets at pH = 0 along  $RuO_2$  for the CER and the OER, respectively [98]. The difference  
 19 in selectivity was attributed to the variation in the adsorption energies of the CER and  
 20 OER intermediates along each facet, which is caused by the disparities in the ligand  
 21 coordination symmetry around each active site that affects the charge distribution and the  
 22 bond length between the adsorbate and active site [98,177].

## 23 IV.2.2. Introducing Point Defects into the Local Chemical Environment

### 24 IV.2.2.1. Lattice Substitution.

25 Exner et al. found in an ab initio thermodynamic study that the activity towards the OER  
 26 could be improved by 0.8 to 1.0 eV by reducing the adsorption energy of oxygen to the  
 27 catalytic  $Ru_{CUS}$  when the ruthenium atoms of the second coordination shell were  
 28 substituted by Ir or Cr [177]. To further their investigation of the OER vs. CER selectivity,

1 Exner et al. found in another study that replacement of the top most monolayer of  
 2  $\text{RuO}_2$  (110) with  $\text{TiO}_2$  improved the CER selectivity by adjusting the bonding strength of  
 3 the oxygen to optimize the strength of the chloride adsorption in the Heyrovsky step [178].  
 4 Karlsson et al. found that monolayers of  $\text{TiO}_2$  on  $\text{RuO}_2$  improved selectivity for the CER  
 5 while maintaining the characteristically high activity of pure  $\text{RuO}_2$ , and that by moreover  
 6 doping  $\text{TiO}_2$  with Ru, the  $\text{Ti}_{\text{CUS}}$  sites could be activated with optimal oxygen adsorption  
 7 descriptor values for active and selective chlorine evolution [179]. Ru has been indeed  
 8 proposed to influence the electronic state of  $\text{TiO}_2$  [180]. Deactivation of DSA electrodes  
 9 was further noted by Karlsson et al. to be caused by the removal of Ru from the surface  
 10 [179,181]. Macounová et al. went one step further to employ a systematic study of spray  
 11 freeze drying prepared nanocrystalline  $\text{Ru}_{1-x}\text{Ti}_x\text{O}_2$  ( $0 < x < 0.2$ ) in chloride containing  
 12 acidic media to dissect the ambiguity surrounding the compositional roles of these  
 13 catalysts within DSA electrodes [182]. The authors found the selectivity towards the CER  
 14 to increase with greater Ti content that relieves Ti clustering along the z axis and promotes  
 15 Ti–Ti pairing between CUS and bridge sites, as shown when comparing Fig. 23a and c;  
 16 these structural shifts were furthermore indicated to cause an increased oxygen  
 17 deficiency within the Ti environment [182]. Moreover, this increased oxygen deficiency  
 18 was indicated to promote the LOM, as evident in the comparison of Fig. 23b and d. Thus,  
 19 the variability in the chlorine selectivity was ascribed to the differences in the mechanisms  
 20 used by the catalyst to evolve oxygen, with catalytic structures that promote the LOM  
 21 having an increased selectivity for the CER [182].



1 Fig. 5: (A) and (B) represent the selectivity ( $\delta$ ) towards chlorine evolution and the tendency to evolve oxygen via the  
2 LOM determined through differential electrochemical mass spectrometry isotopic labeling for  $\text{Ru}_{0.95}\text{Ti}_{0.05}\text{O}_2$ . (C) and (D)  
3 represent the results obtain for the structural composition  $\text{Ru}_{0.80}\text{Ti}_{0.20}\text{O}_2$ . Figure of Macounová et al. [182].

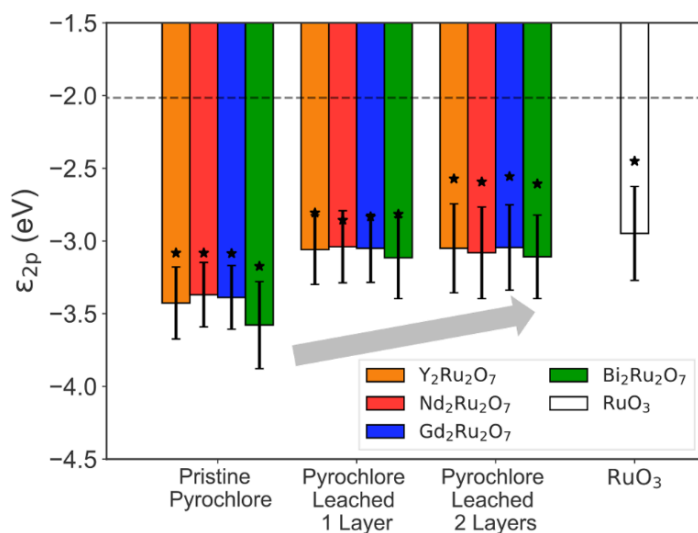
4 In another study, Astudillo et al. found through detection by differential electrochemical  
5 mass spectroscopy that the LOM in acidic, chloride containing aqueous solutions  
6 electrocatalyzed by Ru–Mn–O oxides coincided with greater CER selectivity [183].  
7 However, ab-initio studies indicated that an Ru–Mn–O surface behaves similarly to pure  
8  $\text{RuO}_2$  surface in that the adsorption of oxygen into any conceivable surface site is unlikely  
9 to result in its immobilization that promotes the LOM: the surfaces are rendered too stable  
10 [183]. The binding of oxygen adsorbates at the  $\text{Mn}_{\text{cus}}$  sites was however found to be  
11 weaker, which may promote the migration of a proton towards the bridge sites for the –  
12 OH and –OOH reaction intermediates, and explain the observed experimental trend of  
13 higher OER activity with increasing Mn content [183,184]. However, it must be noted that  
14 spectroscopic confirmation of the CUS and bridge sites in the prepared Ru–Mn–O oxides  
15 remained elusive throughout the study and low dimensionality sites, such as crystal edges  
16 and vertices, were mentioned by the authors to not be taken into account, which may  
17 indeed influence the perceived mechanism of the OER and an understanding of the  
18 observed selectivity [176].

19 Interestingly, substituting  $\text{RuO}_2$  materials with Zn was found to increase selectivity  
20 towards the OER at more positive potentials [185]. The authors suggested that the  
21 substitution resulted in rearrangement of the metal atoms along the [111] that created  
22 more oxygen vacancies on the surface that affected the adsorbate binding of the chlorine  
23 evolution precursors and enhanced the oxygen evolution via the LOM at more positive  
24 potentials [185]. However, the chemical constituent which is substituted into the lattice  
25 may affect the OER mechanism. An overpotential of 214 mV was achieved by Wu et al.  
26 who incorporated Ni into the  $\text{RuO}_2$  lattice; DFT studies and operando electrochemical  
27 mass spectrometry analysis indicated that the Ni replaced Ru in the bridge sites, which  
28 both stabilized the lattice oxygen and promoted the AEM mechanism while achieving  
29 impressive stabilities of >1000 h under a current density of 200  $\text{mA}/\text{cm}^2$  [186].  
30 Interestingly, the oxidation state of the Ru catalyst with Ni embedment was shown through  
31 X-ray photoelectron spectroscopy to be slightly up-shifted compared to  $\text{RuO}_2$ ; higher Ru  
32 oxidation states have been shown to enhance OER electrocatalysis [187]. Moreover, the  
33 number of dopants on the electrocatalytic surface may affect the OER mechanism that  
34 predominates. Zagalskaya and Alexandrov found that substituting the surface of  
35  $\text{IrO}_2$  (110) with only two nickel atoms wasn't enough to induce a mechanistic shift from  
36 the AEM to the LOM [188]. The formation of metal vacancies that were caused by catalyst  
37 dissolution were further proposed to have a synergistic effect with the introduced dopants  
38 to lower the OER overpotential via the LOM [188]. Zagalskaya and Alexandrov further  
39 found defective  $\text{IrO}_2$  to be less LOM active than defective  $\text{RuO}_2$  through simulations  
40 suggesting that by creating two surface vacancies in the high energy 211 facets of  
41  $\text{RuO}_2$  and  $\text{IrO}_2$ , the mechanism could be switched from AEM to LOM in  $\text{RuO}_2$  though not  
42 in  $\text{IrO}_2$ , indicative of the greater structural stability of  $\text{IrO}_2$  under OER conditions [188].

#### 43 *IV.2.2.2. Generating Vacancies within the Lattice.*

44 Incorporating the Ru into a mixed metal oxide such as the pyrochlore  $\text{Pb}_2\text{Ru}_2\text{O}_7$ -  
45  $\times$  structure increased the concentration  $\text{Ru}(\text{V})$  indicated through XPS measurements and

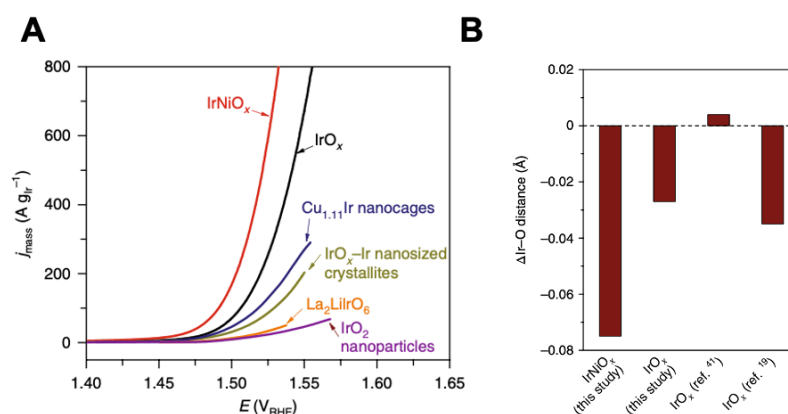
1 was further shown to improve its stability even after being subjected to a 2 h stability test  
 2 in alkaline conditions [189]. The high Ru oxidation state and high concentration of oxygen  
 3 vacancies characteristically present in pyrochlore  $A_2B_2O_{7-x}$  structures that form upon a  
 4 cationic radii mismatch of  $>1.46$  was proposed to promote an improvement in the activity  
 5 and selectively towards the OER during simulated seawater electrolysis under alkaline  
 6 conditions [[190], [191], [192], [193]]. Oxygen vacancies shifted the O-2p orbitals  
 7 upwards, increasing the density of states around the Fermi level and promoting both  
 8 metallic character and potential interaction with AEM adsorbates [190]. Another means of  
 9 generating vacancies within the lattice is through leaching. Though deemed  
 10 thermodynamically unstable under acidic conditions and prone to dissolution through  
 11 cation A-site leaching according to in-situ Pourbaix analysis, an increase in  
 12 electrocatalytic activity with A-site dissolution was found for Ru incorporated into  
 13  $A_2Ru_2O_7$  ( $A = Y, Nd, Gd, Bi$ ) pyrochlores [194]. Weaker interactions between the Ru 4d  
 14 and O 2p orbitals of the OER intermediates of the AEM with longer Ru–O bond lengths  
 15 were shown to improve activity in the materials when compared to  $RuO_2$  [194]. This  
 16 increase in activity was shown to be correlated with both the increase in the density of Ru  
 17 active sites promoted by leaching and an increase in the oxygen 2p-state energy for  
 18 adsorbed oxygen density of states, as shown in Fig. 24 [194]. Moreover, the bulk phase  
 19 of  $Y_2Ru_2O_7$  was shown to be maintained after chronoamperometry testing by XRD and  
 20 also that the surfaces evolves during OER catalysis [194]. The surface coverage of the  
 21 active sites is indeed critical. Gayen et al. found the apparent OER activity of  $Pb_2Ru_2O_{7-x}$   
 22 pyrochlores to decrease upon being subjected to annealing at elevated temperatures  
 23 regardless of the annealing environment; this effect was attributed to the observed  
 24 increase in crystallinity that lowered the density of under-coordinated active sites, which  
 25 decreased their surface coverage on the catalytic surface [189].



26  
 27 Fig. 24. Computed oxygen 2p-state energy comparison of pristine pyrochlore, one and two layer leached pyrochlore,  
 28 and the fully leached pyrochlore-like  $RuO_3$  structure, showing an increasing trend that approaches the computationally  
 29 determined optimal OER activity value of  $-2.0$  eV shown by the dashed line. Figure of Hubert et al. [194].

30 Nong et al. also found that leaching nickel from their  $IrNi@IrO_x$  core-shell nanoparticles  
 31 could achieve uniquely high activities in OER electrocatalysis [195]. The leaching  
 32 produced significantly shortened Ir–O bond lengths at the shell surface with a covalent

1 character that created electrophilic oxygens, highly conductive and more susceptible to  
 2 the nucleophilic attack inherent in the O–O bond formation of the LOM mechanism as  
 3 shown in Fig. 25b. Conclusions from XANES measurements indicated that the iridium  
 4 atoms adjacent to the vacancies formed through nickel leaching had a greater number of  
 5 d-band holes. Moreover, the occupied projected density of states indicated that the iridium  
 6 5d-states were concomitantly lowered below the oxygen 2p states, producing oxygen hole  
 7 formation, with significant Ir character, that was reflected by the appearance of an  
 8 unoccupied, narrow band just above the Fermi level [195].



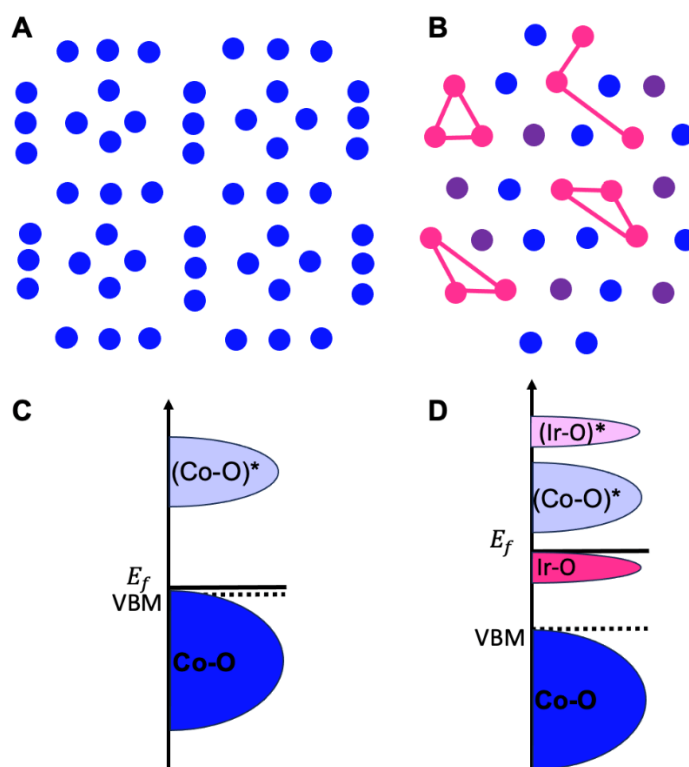
9  
 10 Fig. 25. (A) Comparison of the activity towards the OER in an acidic electrolyte amongst the investigated IrNi@IrO<sub>x</sub>,  
 11 the benchmark IrO<sub>2</sub>, and electrocatalysts of high recorded intrinsic activity divulged from the literature. (B) Degree of  
 12 change in the Ir–O bond length along the surface of the IrNi@IrO<sub>x</sub> nanoparticles, IrO<sub>x</sub> nanoparticles, an IrO<sub>x</sub> film, and  
 13 standard IrO<sub>x</sub> nanoparticles. Figure of Nong et.al. [195].

#### 14 IV.2.3. Use of Single-Atom Catalysts

15 The number and type of atoms within the first and second coordination shell can  
 16 significantly affect the local geometry and charge density of the metal active sites [196]  
 17 Ji. et al. incorporated Ru atoms into a low crystallinity 2D TiO<sub>x</sub> substrate that promoted  
 18 sub-nano ruthenium clusters through a cationic defect adsorption-oxidation anchoring  
 19 method, creating partially oxidized, high valence, and lowly coordinated ruthenium atoms  
 20 [197]. DFT simulations predicted that the CER proceeded through stabilization of the –Cl  
 21 adsorbate by the ruthenium clusters, similar to the results of Lu et al. discussed above,  
 22 avoiding the –OCl intermediate and improving the mass activity, selectivity, and stability  
 23 towards the CER [197]. Though, the close-packed geometries adopted by these  
 24 supported metallic cluster/nanoparticles may limit, as previously indicated, their  
 25 achievable activities and desired selectivities [198].

26 Embedding a metal atom with a heteroatom support as in the case of single-atom  
 27 catalysts (SACs) or amongst adjacent metal atoms, known as correlated SACs (c-SACs)  
 28 may provide greater flexibilities in the structural design to tune the atomic structure and  
 29 the local coordination of the active site to achieve optimal electronic structures for  
 30 selective adsorbate binding with high activities and verified stability [164,198]. Cho et al.  
 31 identified the critical role of the three-coordinated Pt<sup>II</sup> with broken D<sub>4h</sub> symmetry in a  
 32 platinum single atom catalyst with reported CER selectivities approaching 100 % under  
 33 acidic conditions [199]. It must however be understood that the study illustrated the  
 34 significant degree of heterogeneity present at the active sites of SACs and the complexity

1 of discriminating the authentic active sites and the quantifying the intrinsic activity of the  
 2 catalysts through metrics such as the turnover frequency (TOF) [199]. These lowly  
 3 coordinated active sites were deemed more active in the CER than the Pt-N<sub>4</sub> sites  
 4 previously reported with a preferential binding of the –OCI intermediate [199,200]. On the  
 5 other hand, the design and successful synthesis of single atoms that exhibit spatial  
 6 correlation within a sublattice substrate have the potential to exhibit identical structural  
 7 motifs within those substrates. Accommodating iridium single atoms into the cationic sites  
 8 of a cobalt spinel oxide through an ion exchange-pyrolysis procedure produced Ir sites  
 9 that were shown to possess short range order though the partial projected pair distribution  
 10 function profiles derived from multiple high-angle annular dark field scanning high  
 11 resolution transmission electron microscopy (HAADF-HRSTEM) images [201,202].  
 12 These Ir cluster sites exhibited a spatial correlation with the Co<sub>3</sub>O<sub>4</sub> host lattice with the  
 13 majority of the Ir sites exhibiting short range order rather than being isolated within the  
 14 cationic lattice of the Co<sub>3</sub>O<sub>4</sub> [201]. The electrocatalytic active sites were shown to be  
 15 comprised of these short range Ir octahedral spatially correlated sites enclosed by Co  
 16 sites. Electronic structural analysis showed a downshift valence band maximum edge and  
 17 d-band centers of these Ir-Co<sub>oct</sub> nanodomains at the Fermi energy, as shown in Fig. 26d  
 18 that could modulate the oxygen intermediate adsorption energies. An overpotential of 300  
 19 mV at 6 mA/cm<sup>2</sup> was exhibited with a mass activity two orders of magnitude greater than  
 20 commercial IrO<sub>2</sub> catalysts.



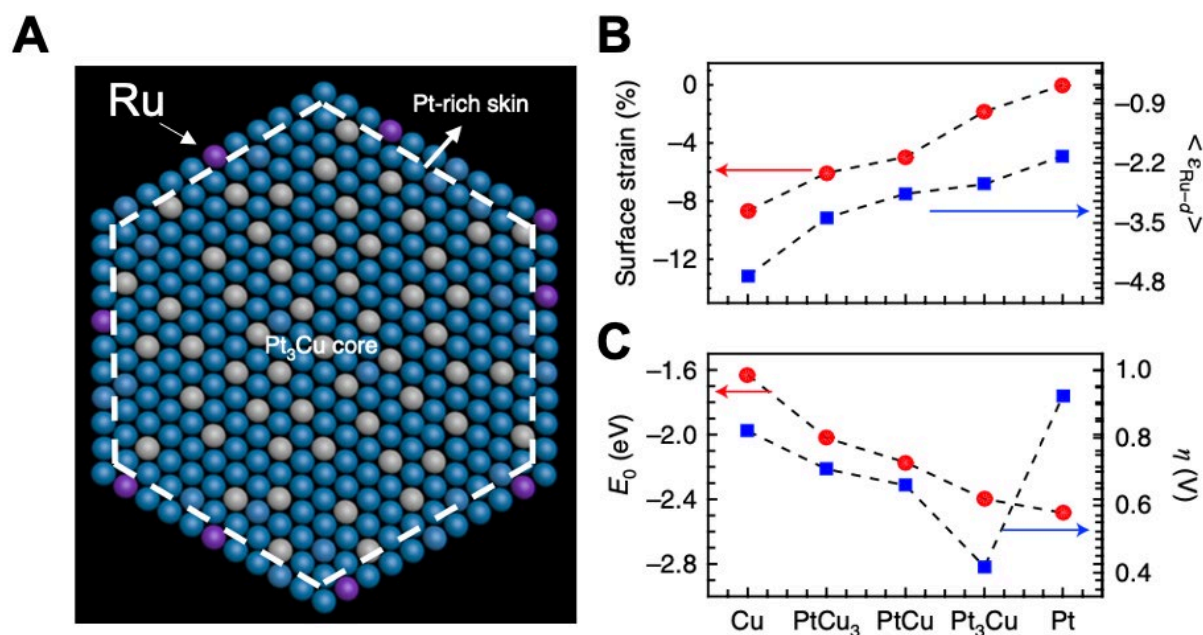
21  
 22 Fig. 26. The schematics of (A) represent the precursor cobalt based zeolitic imidazole framework and (B) the structural  
 23 modification through Ir ion incorporation with correlated sites indicated. The corresponding Density of States diagrams  
 24 are shown in (C) and (D) and reveal the formation of Ir 5d–O 2p states near the Fermi level upon Ir substitution. Figures  
 25 of Shan et al. [201].

26 The activity was also found to be greater than Ir single atoms adsorbed onto a  
 27 Co<sub>3</sub>O<sub>4</sub> support without spatial correlation. Moreover, the electrocatalysis was proposed to



1 proceed through the electrochemical oxide path mechanism, proposed by Antolini [203].  
 2 Chronopotentiometry at a current density of 10 mA/cm<sup>2</sup> showed 200 hrs of continuous  
 3 OER electrocatalysis. Liang et al. further showed that incorporating iridium dopants into  
 4 strontium titanate perovskites could activate the titanium electronic states towards surface  
 5 oxygen adsorption [204]. The intrinsic activity of the catalyst, calculated by normalizing  
 6 the catalytic current by the electrochemical surface area, was found to be 26 times that  
 7 of commercial IrO<sub>2</sub> under acidic conditions. Thus the structural flexibility afforded by  
 8 correlated single atom catalysts could provide an additional metal-metal interaction with  
 9 the means to manipulate the electronic states of the active site to promote selective  
 10 adsorbate binding. The novelty of these discovered electrocatalytic topologies enriches  
 11 the potential development of potent electrocatalysts and requires an ingenuity to tailor the  
 12 active sites with a coordination environment that can achieve the desired selectivity by  
 13 preferentially stabilizing the intermediates and the respective transition states of the  
 14 adsorbate evolution mechanism of the OER for improved stability of the catalyst, or  
 15 promote the -Cl adsorbate pathway of the CER to achieve the desired selectivity at the  
 16 anode to advance the potential of direct seawater electrolysis.

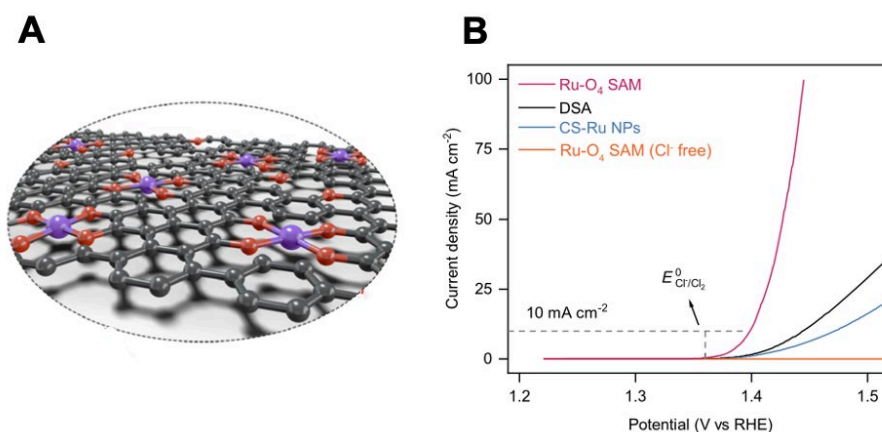
17 The characteristically high OER activity of Ru catalysts is thought to arise from its  
 18 modifiable redox state. The electrocatalytic activity of single atom Ru sites were shown  
 19 to be electronically augmented by incorporating a compressive strain induced by the  
 20 lattice mismatch of the surrounding Pt-rich coordination environment, which shifted the d-  
 21 band center  $\epsilon_{Ru-d}$  towards the Fermi level, optimizing the binding the OER reaction  
 22 intermediates as shown in Fig. 27 [26].



23  
 24 Fig. 27. (A) Representative atomic schematic of the most potent Ru<sub>1</sub>-Pt<sub>3</sub>Cu electrocatalyst in a series of PtCu alloys  
 25 with the position of the Pt in blue, the Cu in grey, and the Ru in purple determined through elemental mapping of the  
 26 HAADF image. (B) indicates the shifting of the  $\epsilon_{Ru-d}$  towards the Fermi level in blue squares as the in-plane lattice  
 27 contraction relative to a pristine Pt (111) surface in red circles decreases. (C) Indicates the corresponding absorption

1 energy ( $E_0$ ) of the oxygen adsorbate and the overpotential ( $\eta$ ) resolved through DFT theoretical analysis. Figures of  
2 Yao et al. [26].

3 ATR-IR measurements further detected the presence of the  $-OOH$  intermediate  
4 suggesting the Ru sites catalyzed the OER through the AEM mechanism, which ensured  
5 stability while also requiring an overpotential of just 220 mV to achieve the metric current  
6 density of  $10 \text{ mA/cm}^2$  under acidic conditions [26]. In situ XAFS and XPS measurements  
7 also revealed the transfer of electrons towards the Ru atom, indicating possible charge  
8 compensation that prevented the over oxidation of the Ru atom and its subsequent  
9 dissolution [26]. Similar redox shifts were seen by Liu et al. who embedded Ru single  
10 atoms in an oxygen coordinated metal organic framework nanosheet shown in, which  
11 downshifted the bonding  $Ru_{3d}$  band center towards the bonding  $O_{2p}$  band and weakened  
12 the chemical bonding between the Ru active sites and the  $-Cl^-$  adsorbate of the CER  
13 more so than the  $-OH$  adsorbate of the OER [205]. This refinement decreased the Gibbs  
14 Free Energy change of the potential determining step of the proposed CER mechanism,  
15 the second Heyrovsky step accompanying the formation of the molecular chlorine, which  
16 enabled the reaction to proceed with a lower overpotential than the OER [205]. The  
17 material demonstrated an overpotential of just 30 mV to catalyze the CER at a current  
18 density of  $10 \text{ mA/cm}^2$  in 1 M NaCl and pH = 1, current densities of  $1000 \text{ mA/cm}^2$  were  
19 further shown to be maintained for >1000 h with a  $Cl_2$  selectivity of >98 % in simulated  
20 seawater [205] (Fig. 28).



21  
22 Fig. 28. (A) Schematic of the synthesized RuO<sub>4</sub> single atom moieties (SAM) with ruthenium in purple, oxygen in red,  
23 and carbon in grey. (B) Polarization curves of the Ru-O<sub>4</sub> SAM, the commercial DSA, carbon-supported Ru  
24 nanoparticles, and the Ru-O<sub>4</sub> SAM in a solution free of chloride ions. The scan rate was 5 mV/sec and the rotation rate  
25 was 1600 rpm within a 1 M NaCl solution at pH = 1. The DSA wasn't stirred, and the chloride free solution consisted of  
26 1 M NaClO<sub>4</sub>. Figure of Liu et al. [205].

27 Moreover, this overpotential is less than the 85 mV reported for commercial DSA, which  
28 also has a recorded  $Cl_2$  selectivity of 95.5 %. Thus a strategy that modulates the valence  
29 of single atom Ru and the relative energies of its d-band centers through optimization of  
30 the coordination environment could enable selective binding of the CER or OER  
31 intermediates and the preferred gas evolving reaction at the anode (Table 2).

1 Table 2. Studied electrocatalysts probed for respective CER and OER activities. (NS) indicates not specified, (UD) is  
 2 undetermined, (N/A) is not applicable, (K) is Khrishtalik, (V-H) is Volmer Heyrosky, (AEM) is Adsorbate Evolution  
 3 Mechanism, (LOM) is Lattice Oxygen Mechanism.

Active Site	Crystal Structure	Probed Plane	(+) Substitution (-) Vacancies	Probed Reaction	Preferred Mechanism	Ref.
Ru (CUS)	Rutile RuO <sub>2</sub>	100 & 110	N/A	OER	(100)	183
Ru (CUS)	Rutile RuO <sub>2</sub>	230 & 100	N/A	CER	K (230)	184
Ru (CUS)	Rutile RuO <sub>2</sub>	101	N/A	OER and CER	V-H (-OCl)	187
Ru (CUS)	Rutile RuO <sub>2</sub>	101	N/A	OER and CER	V-H (-OCl)	103
Ru (CUS)	Rutile RuO <sub>2</sub>	001	N/A	OER and CER	AEM	103
Ru (CUS)	Rutile RuO <sub>2</sub>	110	(+) Ir or Cr	OER	AEM	188
Ru (CUS)	Rutile RuO <sub>2</sub>	110	Top Layer TiO <sub>2</sub>	OER and CER	V-H (-OCl)	189
Ti (CUS)	Rutile TiO <sub>2</sub>	110	(+) Ru	CER	V-H (-OCl)	190
UD	Rutile RuO <sub>2</sub>	NS	(+) Ti	CER	NS	193
Ru (CUS) and Mn (CUS)	Rutile RuO <sub>2</sub>	NS	(+) Mn	OER	AEM	194
NS	Rutile RuO <sub>2</sub>	NS	(+) Zn	OER	LOM	196
Ru (CUS)	Rutile RuO <sub>2</sub>	NS	(+) Ni	OER	AEM	197
Ru (CUS)	Rutile RuO <sub>2</sub>	110	(+) 2 Ni	OER	AEM	134
Ru (CUS)	Rutile RuO <sub>2</sub>	110	(+) 6 Ni	OER	LOM	134
Ru	Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-x</sub>	NS	(-) O	OER	AEM	200
Ru	A <sub>2</sub> Ru <sub>2</sub> O <sub>7</sub>	NS	(-) A = Y, Nd, Gd, Bi	OER	AEM	204
Ir-O	IrNi@IrO <sub>x</sub>	N/A	(-) Ni	OER	LOM	205
Ru	2D TiO <sub>x</sub>	N/A	N/A	OER and CER	V-H (-Cl)	207
Pt-N <sub>4</sub>	CNT	N/A	N/A	OER and CER	V-H (-OCl)	209
Ir	Co <sub>3</sub> O <sub>4</sub>	N/A	N/A	OER	ECOP by Antolini [213]	211
Ru	Pt <sub>3</sub> Cu	N/A	N/A	OER	AEM	51

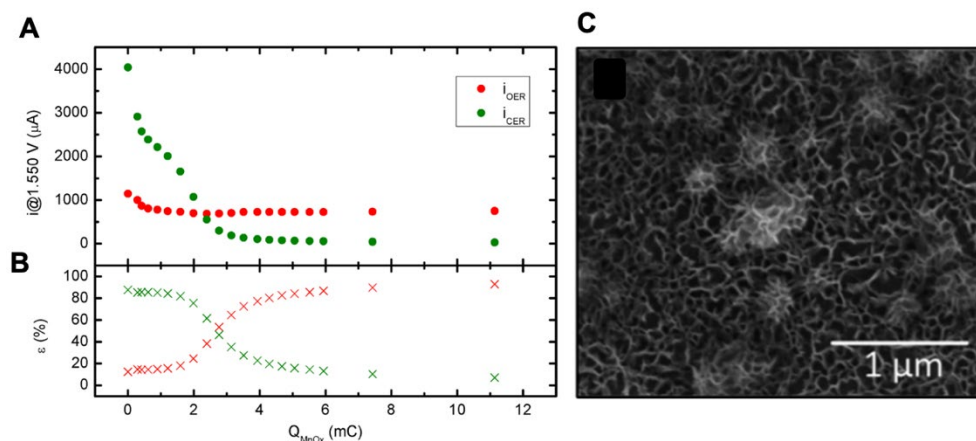
Ru	MOF	N/A	N/A	OER and CER	V-H (-Cl)	215
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### 1 IV.3 In-Situ Filtration

2 The evolution of chlorine may also be impeded by arresting the species transport of the  
3 chloride ions towards the anode. Strategies such as the application of an  
4 electrochemically inert coating layer with an optimized thickness that selectivity mitigates  
5 the respective concentrations of the desired reactants and products at the buried  
6 interface, and renders a physical stability resistant to delamination; the incorporation and  
7 synthetic linkage of electrostatic repelling polyanion moieties; the degree of crystallinity  
8 of electrocatalytic surfaces; and the placement of a gas-permeable, hydrophobic  
9 membrane between the seawater and the anode have all been designed to impede the  
10 species transport of the chloride ion and selectively evolve oxygen at the anode during  
11 seawater electrolysis.

12 Initially implemented by Bennett, a layer of MnO<sub>2</sub> was electrochemically deposited onto a  
13 DSA substrate and shown to evolve oxygen from seawater with 99+% efficiency [206].  
14 He further proposed that the coating layer prevented the diffusion of chloride ions,  
15 creating a polarized concentration gradient. Subsequent studies by Fujimura et al.  
16 deposited MnO<sub>2</sub> on an IrO<sub>2</sub>-coated titanium plate with 13 mol% molybdenum; the film was  
17 found to consist of a single phase of δ-MnO<sub>2</sub> that only slightly reduced the activity towards  
18 oxygen evolution while improving the durability of the material to reach an OER efficiency  
19 of 98.5 % for over 1500 h in pH = 12 at 1000 A/m<sup>2</sup> [74]. Further additions of tungsten were  
20 conducted by Habazaki et al., who found the manganese-molybdenum-tungsten oxide  
21 anodically deposited on an IrO<sub>2</sub>-coated titanium improved the activity of the electrode  
22 towards the OER [207]. Moreover, additions of iron by Ghany et al. to an Mn-Mo oxide  
23 anodically deposited on an IrO<sub>2</sub> coated Ti substrate was shown to improve the stability of  
24 the material at higher temperatures while maintaining 100 % OER efficiency [208].

25 Intrigued by the impressive OER selectivity characteristic of these manganese oxide  
26 based overlayers, Vos et al. electrochemically grew a thin film (5 – 20 nm) of MnO<sub>x</sub> on a  
27 GC disk electrode with a IrO<sub>x</sub> catalytic layer and used rotating ring-disk electrode  
28 voltammetry to discover that the selectivity for the CER at 30 mM Cl<sup>-</sup> decreased from 86  
29 % to 7 % in the presence of the MnO<sub>x</sub> overlayer, though with a 45 % drop in activity for  
30 the OER [209]. The morphology of the overlayer consisted of a porous structure of  
31 intertwined, amorphous sheets of δ-MnO<sub>2</sub> with a thickness of 8–10 nm that were thought  
32 to be electrochemically inert and instead impeded the species transport of the chloride  
33 ion while remaining permeable to H<sub>2</sub>O, H<sup>+</sup>, and O<sub>2</sub> as shown in Fig. 29 [209]. Thus at the  
34 buried interface between the MnO<sub>x</sub> and the IrO<sub>x</sub> catalytic layer, the diffusion coefficient  
35 and concentration gradient of the chloride ion are decreased, increasing the diffusion  
36 layer thickness and the overpotential required for the chlorine evolution.

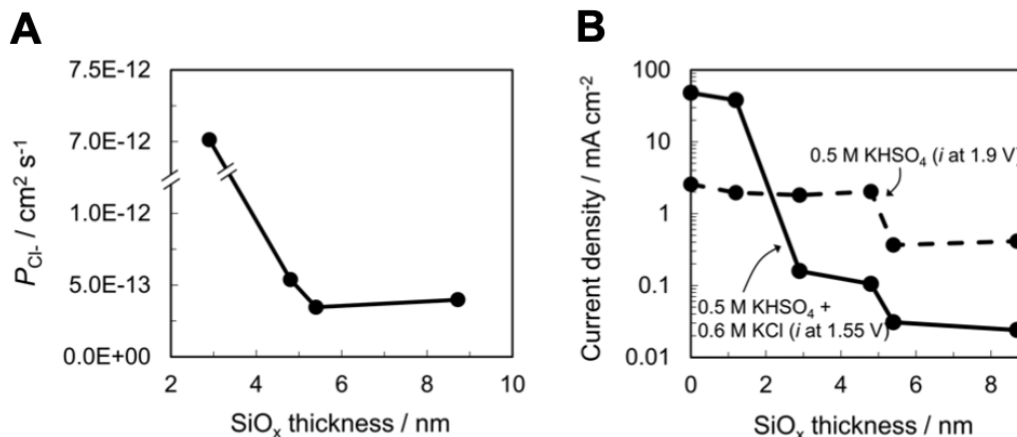


1  
 2 Fig. 29. (A) OER and CER recorded currents at 1.550 V calculated with the rotating ring disk electrode indicating a  
 3 drop in CER currents as the charge (Q) characteristic of the MnO<sub>x</sub> layer thickness is increased, a 45 % decrease in  
 4 the OER activity is also evident. (B) The equivalent selectivities of the OER and the CER as a function of the charge  
 5 of the MnO<sub>x</sub> layer. (C) SEM image of thin, porous sheets of MnO<sub>x</sub> deposited on the IrO<sub>x</sub> / GC electrode. Figure of Vos  
 6 et al. [209].

7 Beatty et al. initiated a study of the structure-property relation of the buried interface; the  
 8 induced confinement effects may indeed affect the steric, chemical, and electronic  
 9 properties of the mechanistic intermediates and may enable an addition means of tuning  
 10 the activity and selectivity of the desired reaction [210]. Different thicknesses of  
 11 SiO<sub>2</sub> overlayers were grown on Pt substrates of varying thicknesses. Silica is considered  
 12 more thermodynamically stable in acidic and neutral solutions under a wider range of  
 13 applied potentials than manganese oxide [211]. Through measurements of the hydrogen  
 14 underpotential deposition ( $H_{\text{upd}}$ ) by cyclic voltammetry, the peak in the voltammogram at  
 15 +0.26 V RHE typically associated with Pt (100) terraces could be found for the 4.6 nm  
 16 SiO<sub>x</sub> overlayer on thick Pt substrate, though was greatly suppressed in the  
 17 voltammograms of the bare Pt control and the 1.4 nm SiO<sub>x</sub> overlayer thickness, and  
 18 skewed in the 10.3 nm SiO<sub>x</sub> overlayer due to slow proton diffusion through the overlayer,  
 19 indicating that the Pt crystal orientation and densities of the crystalline defects can be  
 20 modulated by the thickness of the overlayer, providing a potential means to select for the  
 21 CER or OER [210]. Moreover, the thickness and composition of the Pt oxide interlayer,  
 22 shown to be grown between the SiO<sub>x</sub> overlayer and the Pt thin film through XPS  
 23 measurements, was found to be tunable by adjusting the thicknesses of the  
 24 SiO<sub>x</sub> overlayer and Pt/Ti substrates; these characteristics were furthermore found to  
 25 dictate electrochemical properties, the stability of the SiO<sub>x</sub> overlayers, and the HER  
 26 performance [210]. Indeed, a reduction in the thickness of the interlayer can rupture the  
 27 steric environment between the interlayer and the silica overlayer, even affecting the  
 28 potential mechanism. Robinson et al. moreover found that application of SiO<sub>x</sub> overlayers  
 29 on a platinum thin film disposes adjacent silanol groups at the Pt active centers that can  
 30 facilitate the oxidation of the CO intermediates that have adsorbed onto Pt to CO<sub>2</sub>,  
 31 advancing the potential of fuel cells that directly utilize alcohols [212].

32 To thus further the applicability of silica overlayers towards selective OER catalysts,  
 33 Bhardwaj et.al. applied a SiO<sub>x</sub> overlayer on a thin Pt film electrode; the 4.8–8.7 nm  
 34 overlayer thicknesses demonstrated a three order of magnitude decrease in the

1  $\text{Cl}^-$  permittivity when compared to aromatic polyamide membranes utilized in reverse  
2 osmosis water desalination membranes as shown in Fig. 30 [21].

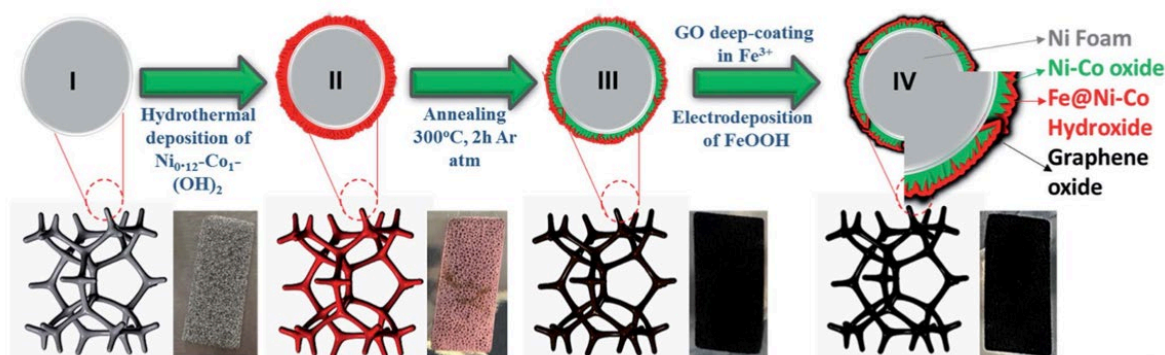


3  
4 Fig. 30. (A) Calculated permeability of  $\text{Cl}^-$  through an  $\text{SiO}_x$  overlayer deposited on Pt thin film electrocatalyst as a  
5 function of the  $\text{SiO}_x$  overlayer thickness as determined through linear scanning voltammetry in 0.5 M  $\text{KHSO}_4 + 0.6$  M  
6  $\text{KCl}$ . (B) The current densities recorded during linear scanning voltammetry at +1.90 V vs. RHE in 0.5 M  $\text{KHSO}_4$  in the  
7 dotted curve and at +1.55 V vs. RHE in 0.5 M  $\text{KHSO}_4 + 0.6$  M  $\text{KCl}$  in the solid curve. Figure of Bhardwaj et al. [21].

8 The selective transport arresting mechanism was proposed to be the additional energy  
9 required to rearrange the bonds of the hydration sphere surrounding the chloride ion,  
10 which required removal to permeate the free volume elements within the  $\text{SiO}_x$  overlayer,  
11 determined by ellipsometric porosimetry measurements and XPS analysis to have Si-Si  
12 nearest neighbor distances of  $\sim 4.6$  Å [21]. Indeed, the hydrated diameters of the  $\text{Cl}^-$  ion  
13 has been measured to be 6.5 Å [213]. Vos et al. furthered this study by also applying the  
14  $\text{SiO}_x$  overlayers on amorphous iridium oxide nanoparticles and iridium mixed-metal  
15 oxides deposited on a Ti support and found the morphology of the underlayer and its  
16 synergy with the overlayer to be of crucial importance towards achieving both a selective  
17 and stable electrocatalytic design [214]. Microscopic defects and irregularities in the  
18  $\text{IrO}_x$  nanoparticle substrate indeed affected the electrocatalytic selectivity towards the  
19 OER and no correlation between the overlayer thickness and OER selectivity could be  
20 found [214]. Silica overlayers applied on the mixed metal substrate appeared to decrease  
21 the activity for both the CER and the OER, though were more favorable towards the OER  
22 with prolonged integrity maintained during a potentiodynamic electrolysis evaluation  
23 [214].

24 Iridium oxide coated titanium substrates have also been hot pressed with the cation  
25 selective perfluorosulfonic acid polymer Nafion® [215]. Though achieving lower current  
26 densities, applying a Nafion-117 membrane ( $\text{H}^+$ -form) onto the coated electrode allowed  
27 water to permeate while electrostatically repelling the chloride ions and led to nearly 100  
28 % oxygen selectivity at pH = 8.3. A similar sieving mechanism with the use of the anionic  
29 backbone of sulfonated polystyrene-block-(ethylene-ran-butylene)-block- polystyrene  
30 polymer (S-PSEBS) was applied to coat an  $\text{IrO}_2/\text{Ti}$  anode with an electrostatically  
31  $\text{Cl}^-$  repelling layer [216]. The sulfonated form of the S-PSEBS polymer, with a  
32 hydrophilicity that enables the species transport of water molecules, was shown to  
33 increase the oxygen evolution efficiency to 94 % and decrease the chlorine evolution  
34 efficiency to 6 % at 100  $\text{mA/cm}^2$  at pH = 8.3.

1 Selective electrocatalysts have also been designed for alkaline conditions with a  
 2 graphene oxide overlayer that was electrodeposited with iron hydroxide onto an  
 3 annealed, porous nickel foam that had been subjected to a hydrothermal deposition of  
 4 Ni-Co hydroxide as shown in Fig. 31 [217]. The electrocatalyst was able to reach current  
 5 densities of  $1 \text{ A / cm}^2$  under alkaline conditions below overpotentials reaching 480 mV  
 6 and thus before the evolution of hypochlorite becomes thermodynamically possible [217].  
 7 The graphene oxide overlayer was shown to improve the resistance to corrosion caused  
 8 by the chloride ion, and moreover improve the OER activity both by decreasing the size  
 9 of the FeOOH nanoparticles, and thus improving their interaction with the Ni-Co hydroxide  
 10 underlayer, and by decreasing the charge transfer resistance of the material, and thus  
 11 improving its electrical conductivity [217].

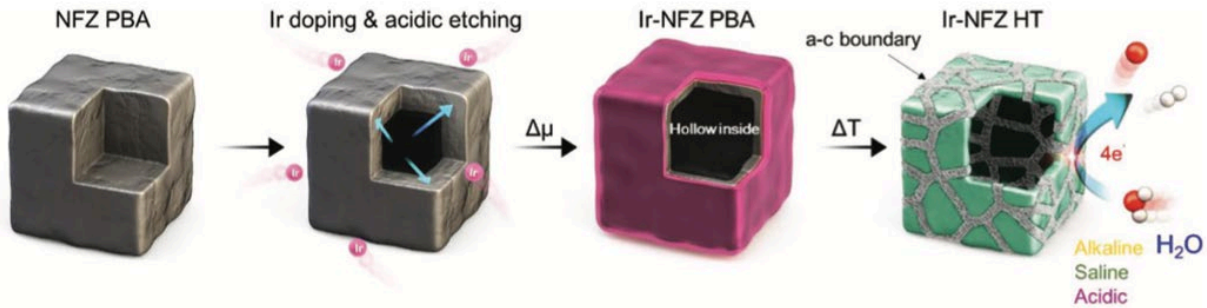


12  
 13 Fig. 31. Schematic depiction of the FeOOH deposited on  $\beta$ -Ni-Co hydroxide with a graphene oxide outer layer. Figure  
 14 of Jadhav et.al. [217].

15 Kitiphatpiboon et al. found that by submerging a nickel foam that had been oxidized to  
 16 form  $\text{NiFe(OH)}_x$  along its surface into a 0.1 M  $\text{Na}_2\text{S}$  solution for sulfur integration, the  
 17 stability of the electrode could be improved by the intercalation of sulfate ions, which could  
 18 block the species transport of the chloride anions [218]. The sulfur doping was also shown  
 19 to improve the conductivity between the active sites on  $\text{FeNiS}_x$  and  $\text{NiFe(OH)}_x$  [218]. A  
 20 strategy that prepared porous N-NiMo<sub>3</sub>P sheets with negatively charged surface  
 21 polyanions such as nitrates and phosphates also protected the electrode from the chlorine  
 22 chemistry [219]. Alternatively, Obata et al. utilized anodic deposition to apply a  
 23  $\text{CeO}_x$  overlayer onto an Au substrate that had been coated with  $\text{NiFeO}_x$  through  
 24 conventional cathodic deposition and found that the overlayer prevented dissolution of  
 25 the active Fe species and selectively impeded the chloride ion through an electrostatic  
 26 interaction [220]. With an isoelectric point of 7,  $\text{CeO}_x$  is expected to be negatively charged  
 27 under alkaline conditions [220]. Its hydrous, disordered structure was proposed to enable  
 28 the diffusion of  $\text{OH}^-$  to the  $\text{NiFeO}_x$  catalyst on the Au substrate, promoting an OER  
 29 overpotential shown to be less than the onset of the hypochlorite redox potential  
 30 [220,221].

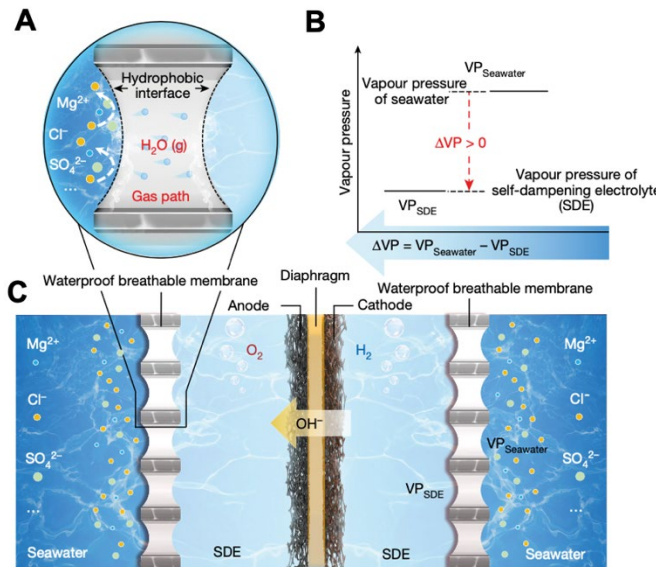
31 Interestingly, a hollow nanocubic electrocatalyst composed of Ir-doped Ni-Fe-Zn Prussian  
 32 blue analogs was demonstrated to manifest abundant amorphous-crystalline interfaces  
 33 (ACI) that were indicated to be in-situ passivated with carbonate anions after prolonged  
 34 electrolysis in an alkaline seawater electrolyte [222]. These carbonate anions were  
 35 proposed to protect the electrocatalyst against chloride corrosion by repelling the  
 36 negatively charged chloride anions. The synthesized hollow nanocubes were further

1 shown to have a higher catalytic activity than commercial  $\text{IrO}_2$  in alkaline, alkaline  
 2 seawater, and acidic electrolytes that was proposed to be facilitated by the heterogeneity  
 3 of atomic arrangements at the ACI surface as shown in Fig. 32 [222]. The Zn was however  
 4 shown to be completely leached out under acidic conditions, though a synergy between  
 5 the Ni, Fe, and Ir at the surface of the nanocubes was supposed to preserve the ACI  
 6 during water oxidation.



7  
 8 Fig. 32. Schematic representation of the synthetic route utilized to generate the numerous amorphous-crystalline  
 9 interfaces on the Ir-NFZ HT nanocube. Figure of Han et al. [222].

10 Xie et al. further designed a hydrophobic, porous polytetrafluoroethylene (PTFE) based  
 11 membrane permeable only to gases that encompassed the anode and sandwiched a  
 12 concentrated KOH solution, termed a self-dampening electrolyte, that provided a water  
 13 vapor pressure gradient driving the evaporation and diffusion of water vapor from the  
 14 seawater across the PTFE membrane towards the catalyst at the anode as shown in Fig.  
 15 33 [223]. Current densities of  $250 \text{ mA/cm}^2$  with an operational lifetime of over 3200 h were  
 16 achieved [223].



17  
 18 Fig. 33. (A) Schematic of the hydrophobic porous polytetrafluoroethylene (PTFE)-based waterproof breathable  
 19 membrane permitting the selective diffusion of water vapor while remaining impermeable to impurity ions and  
 20 seawater. (B) Representation of the driving force created for water vapor diffusion through application of a self-

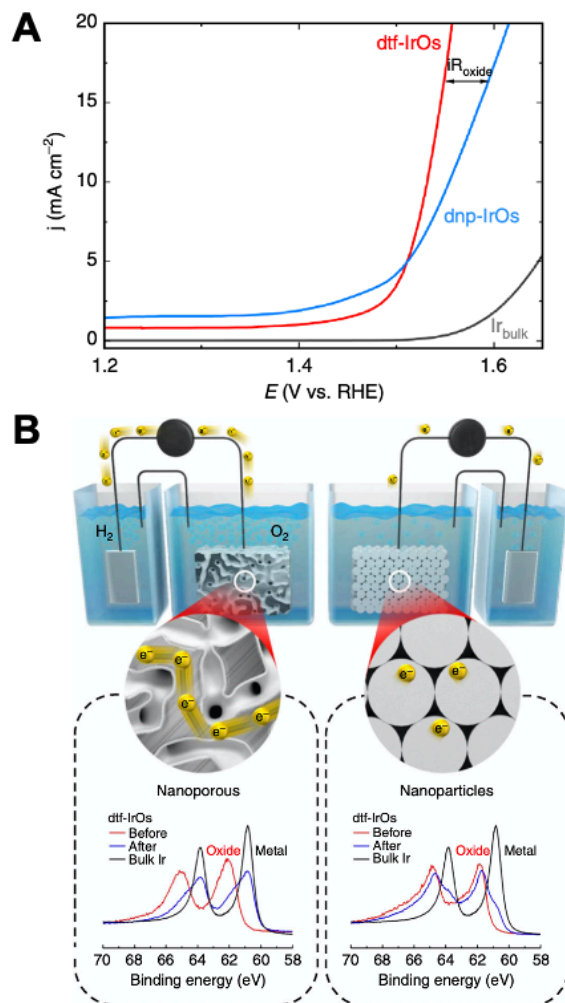


1 dampening electrolyte. (C) Depiction of the orientation of the membrane and the electrolyte with respect to the anode  
2 and the cathode. Figure of Xie et al. [223].

3 The use of the membrane within the electrolyzer unit itself could moreover act as a filtering  
4 mechanism to prevent the movement of the chloride ion towards the anode. Though an  
5 asymmetric electrolyzer design, Shi et al. introduced natural seawater into the cathode  
6 compartment and a hydroxide solution into the anode compartment; the species transport  
7 of the chloride ion was impeded from approaching the anode through the placement of a  
8 sodium ion exchange membrane [224]. The Ni-Fe-P nanowires anchored with atomically  
9 dispersed Pt at the cathode accelerated hydrogen evolution through a DFT calculated  
10 energy barrier reduction of 0.26 eV in natural seawater [224].

#### 11 IV.4 Augmenting the Conductivity

12 By manipulating the surface structure of the catalyst, an augmentation in the conductivity  
13 may be realized, which may indeed lower the overpotential required to effectuate the OER  
14 and enable selectivity against the CER to be achieved under acidic conditions.  
15 Conductivity is related to the concentration of mobile electronic carriers such as electrons,  
16 holes, and ionic point defects occupying lattice atomic positions such as vacancies,  
17 interstitials, and substitutional solutes as well as impurities [225]. Indeed, removing  
18 oxygen atoms through mechanisms such as the Mars-van Krevelen leaves excess  
19 electrons either delocalized through a metallic state or localized within a polaronic state  
20 [226]. The mobility of these electronic carriers is defined as the velocity of the entity per  
21 unit driving force and is directly proportional to the diffusion coefficient according to the  
22 Nernst-Einstein relation. In addition, electrons and holes in metals, semiconductors, and  
23 high-mobility ceramics are subject to a drift velocity that is much less than the  
24 instantaneous velocity of random particle movements. Their mobility is inversely  
25 proportional to their effective mass, which considers the interaction between the charge  
26 carrier and the lattice potential [225]. This polaronic interaction may be large, which  
27 indicates a weak interaction between the carrier and the ion and a small effective mass,  
28 or strong resulting in large polarons in which the motion of electrons and holes must occur  
29 through a thermally activated hopping mechanism and can reduce mobility [225]. Kim et  
30 al. synthesized an IrO<sub>2</sub> shell encasing a metallic iridium core by rapidly dealloying osmium  
31 from an Ir<sub>25</sub>Os<sub>75</sub> alloy under highly acidic conditions [121]. A decrease in overpotential for  
32 the Ir<sub>25</sub>Os<sub>75</sub> core-shell thin film when compared to a synthesized Ir<sub>50</sub>Os<sub>50</sub> nanoparticle at  
33 high current densities is shown in Fig. 34a, which was attributed to the measured increase  
34 in conductivity [121]. The conductivities of the 3D-interconnected, porous Ir<sub>25</sub>Os<sub>75</sub> core-  
35 shell thin film and the Ir<sub>50</sub>Os<sub>50</sub> nanoparticles, proposed to be highly oxidized and  
36 consisting of many insulating oxide interfaces, were quantified through measurements of  
37 the carrier mobility and carrier density with 4-probe van der Pauw measurements [121].  
38 The interconnected heterogeneity of a metallic core oxide shell structure could indeed  
39 create additional undercoordinated sites that induce alterations in the local geometries,  
40 the electronic structures, and additional defect sites that can be manipulated to tailor the  
41 electrocatalytic properties of the surface [226].



1  
 2 Fig. 34. (A) Linear sweep voltammogram with a rotating disk electrode in 0.1 M HClO<sub>4</sub> showing the polarization curves  
 3 of the Ir<sub>25</sub>Os<sub>75</sub> core-shell material (dtf-IrOs) and Ir<sub>50</sub>Os<sub>50</sub> nanoparticle (dnp-IrOs). (B) A depiction of the effect of  
 4 numerous, insulating oxide interfaces on the conductivity of the material; the oxides layers were quantified through XPS  
 5 sputter etching experiments. The XPS experiments for the dtf-IrOs material indicated on the other hand the presence  
 6 of an Ir-metallic core. Figure of Kim et al. [121].

7 Indeed, induction of polaronic interactions with the CO adsorbate in the rutile titanium  
 8 dioxide (110) was shown to significantly affect its adsorption energy and the polaronic  
 9 ground state of the system; CO adsorption was shown to promote polaron transfer from  
 10 subsurface to surface sites [227]. Probed through analysis of the polaron formation  
 11 energy, or the electronic energy gained by phonon-electron coupling balanced the energy  
 12 lost to local lattice distortions, the CO adsorbate was shown to not only reduce the energy  
 13 cost to form the polaron though also was found to bind most favorably at a titanium atom  
 14 site with a polaron just below [227].

15 Stoerzinger et al. manipulated the degree of epitaxial strain within a LaCoO<sub>3</sub> thin film  
 16 grown through pulsed layer deposition on insulating substrates of different thicknesses  
 17 and found the degree of tensile strain to influence the electrical conductivity and observed  
 18 activity towards the OER; deviations in the local symmetry were proposed to affect the  
 19 number of defects sites and the charge transfer resistance, and moreover to decrease

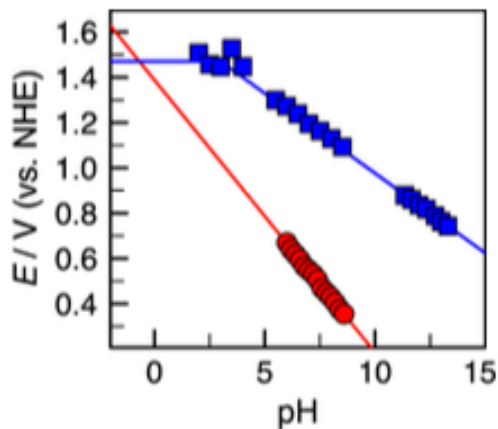
1 the Co–O bond distance and increase the strength of the adsorbed bond to oxygen [228].  
2 Engineering these defects were moreover shown to dramatically improve the OER  
3 performance of a Co-doped nanorod-like RuO<sub>2</sub> electrocatalyst; the low oxidation state of  
4 the Co dopant required less O<sup>2-</sup> in the RuO<sub>2</sub> lattice and thus yielded oxygen vacancies,  
5 as evidenced through X-ray photoelectron spectroscopy analysis [229]. The oxygen  
6 vacancies were proposed to improve not only the electrical conductivity of the materials  
7 though also augment the number of active sites, and moreover participate in the LOM  
8 mechanism, calculated to be the lowest free energy path according to DFT simulations  
9 [229]. Overpotentials of 169 mV for the OER under acidic conditions were achieved with  
10 stable chronopotentiometry measurements for over 50 h at 10 mA/cm<sup>2</sup> [229]. Thus  
11 strategies that implement designs to elevate the conductivity of the electrocatalyst at the  
12 active site through formation of point defects and manipulation of the electronic structure  
13 have the potential to tune the binding of the preferential intermediate and moreover  
14 promote the activity of the material without depreciating the inherent stability.

#### 15 IV.5 Self-Healing Catalysts

16 Tuning the catalytic active site and the reaction mechanism selectivity is indicated within  
17 to be quite challenging through heterogeneous electrocatalysis of PGM metals. Though  
18 the high anodic potentials required to effectuate the OER and the resulting harshly acidic  
19 environment has generally required a characteristically robust catalyst such as a  
20 heterogeneous catalyst composed of PGM metals in PEMWE technology [230]. Indeed,  
21 oxides of earth-abundant metals are basic according to the Lux classification of bases,  
22 and thus readily react with acid and corrode through leaching and dissolution [231].  
23 Implementation of molecular electrocatalysts to facilitate the OER can on the other hand  
24 enable the structure-activity relationships and reaction mechanisms to be finely tuned  
25 through manipulation of the ligand design [230]. However, most of the ligand design  
26 optimizations to impart selective activity of the metal center such as metathesis, transfer  
27 dehydrogenation, C–H activation and functionalization, and cross coupling bond  
28 formation have been developed under reductive conditions, requiring the development of  
29 ligands stable to oxidative transformations [232].

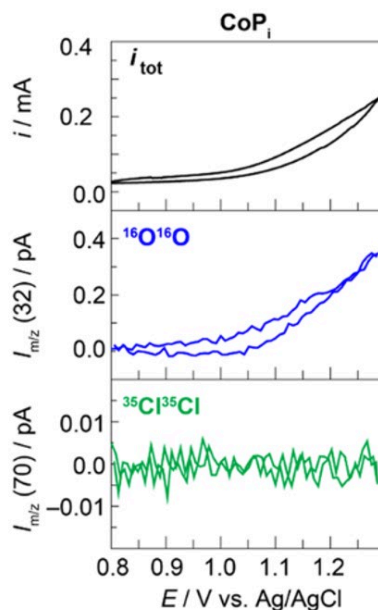
30 One approach to catalyst design can be the development of molecular electrocatalysts  
31 which undergo self-healing, the characteristic ability to reform from a self-assembly  
32 process [233]. If the equilibrium for self-assembly energetically lies within that of the OER  
33 catalysis, overall corrosion of the catalyst can be avoided [233]. Indeed, regeneration will  
34 occur if the catalyst can self-assemble at applied potentials lower than the potentials  
35 required to effectuate the OER. If a greater dependence on the proton concentration  
36 through calculation of its reaction order within the mechanism is moreover found for the  
37 self-healing catalyst than for the catalysis of the OER, pH adjustments can be utilized to  
38 selectively tune the propensity towards self-assembly while maintaining catalytic  
39 functionality [233]. Huynh et al. electrodeposited manganese oxide (MnO<sub>x</sub>) onto an FTO  
40 working electrode and determined its catalytic rate law for the OER through assessments  
41 of the Tafel slopes and the reaction order with respect to the proton concentration at acidic  
42 and basic pH values [234]. Reformulations of the Tafel plots to a single potential (E) vs.  
43 pH plot, shown in Fig. 35, with an additional MnO<sub>x</sub> deposition trace under acidic [235] and  
44 slightly basic conditions [236] enabled a prediction of the pH conditions in which catalyst  
45 regeneration subsides and a net dissolution of the film commences [234]. The self-healing

1 property of the  $\text{MnO}_x$  catalytic film, shown to evolve through the disproportionation  
2 reaction of two  $\text{Mn}^{+3}$  ions, was indeed indicated to uphold until a pH of 0 was approached.



3  
4 Fig. 35. The potential required for the evolution of oxygen on  $\text{MnO}_x$  (blue squares) as a function of the pH showing a  
5 zero-order dependence on the proton concentration under acidic conditions and the inverse first-order dependence in  
6 the alkaline regime. The red trace indicates the fourth-order dependence of  $\text{MnO}_x$  deposition on the proton  
7 concentration under acidic and near neutral pH regimes that were divulged from the literature. The concentrations of  
8  $\text{Mn}^{+2}$  under both measurements are comparable. Figure of Huynh et al. [234].

9  
10 Surendranath et al. further showed that cobalt phosphate ( $\text{CoP}_i$ ) was capable of self-  
11 healing; electrodeposition of the oxidic metallate onto a FTO electrode achieved an  
12  $\text{O}_2$  faradaic efficiency of near 100 % in neutral salt water [237]. The high activity of this  
13 catalyst towards the OER in neutral pH conditions was further proposed to improve the  
14 selectivity against the CER, which according to the Pourbaix analysis discussed above,  
15 becomes thermodynamically unfavored as the pH increases and the OER becomes more  
16 thermodynamically preferred [238]. Though more importantly, selectivity against the CER  
17 was shown to be achieved by engaging the kinetic competition between the water and  
18 chloride ion through exposure of the catalytic edge sites of the metallate cluster present  
19 in the  $\text{CoP}_i$  complexes [238]. The large disparity between the concentration of water and  
20 that of chloride ions in solution can promote the substitution of  $\text{P}_i$  for water to initiate the  
21 O–O bond formation. The effectiveness of this strategy to achieve selectivity is seen  
22 in Fig. 36, where differential electrochemical mass spectrometry (DEMS) was used to  
23 determine the quantities of oxygen and chlorine evolved at pH = 7.



1  
2 Fig. 36. The top panel is a cyclic voltammogram of  $\text{CoP}_i$  in an aqueous solution of 100 mM  $\text{KPi}$  and 500 mM  $\text{NaCl}$  at a  
3 scan rate of 5 mV/s. The middle and bottom panels are the DEMS results for the evolved oxygen and the evolved  
4 chlorine, respectively. Figure of Kean and Nocera [238].

5 The presence of phosphate in the solution was moreover shown to decrease the faradaic  
6 efficiency for the CER through both its buffering effect and ability to associate with oxide  
7 surfaces through an inner-sphere mechanism and form a negatively-charged electrically  
8 repelling layer [239]. Applying the ingenuity of this advancement towards the design of  
9 heterogeneous electrocatalysts selective for the OER that are imbued with the propensity  
10 for self-healing under acidic conditions would engender a robust solution for PEMWE  
11 technology.

## 12 V. Conclusions

13 A social-technological crisis has emerged as the energy demands of our increscent  
14 societies encroach on limited freshwater reserves. It is urgent to develop the capability of  
15 utilizing the abundant reserves of seawater in sustainably driven water electrolyzers for  
16 the generation of hydrogen. While indirect electrolysis may provide the needed short-term  
17 solution, the inevitable additional energy costs will prove absorbent over the long term.  
18 The advancement of direct seawater technologies that further the selectivity of the anode  
19 may improve wastewater treatments, appeasing the exigencies for water conservation  
20 imperative for an increasing percentage of our inhabited world. Though utilizing seawater  
21 directly in the current state-of-the-art electrolyser technologies can affect its performance  
22 both at the system and stack level by degrading the electrolyser durability. Specifically,  
23 the presence of the chloride ion enables the evolution of the toxic and corrosive chlorine  
24 gas. Using seawater as an electrolyte can also affect the electrochemically active  
25 dimensions of the catalyst and perturb the electrolyte permeabilities, diffusivities,  
26 conductivities, and vapor pressure, impacting the current and voltage efficiencies.

27 Thermodynamic analysis of the Pourbaix diagram for artificial seawater indicates that the  
28 competition between the oxygen evolution and chlorine evolution is exacerbated in the  
29 acidic medium of PEM electrolyzers. Nonetheless, in this condition the highest current

1 densities have been achieved. Butler-Volmer kinetics and Marcus theory clarifies the  
2 relation between the thermodynamics and the kinetics of electrochemical reactions,  
3 enabling an understanding of the observed chlorine gas evolution at the anode. Despite  
4 the greater standard potential of the CER, the reaction proceeds through a single  
5 intermediate that enables chlorine evolution to be the kinetic product during seawater  
6 electrolysis. The proposed mechanisms of the OER were elucidated and indicated that  
7 the LOM mechanism can affect the stability of the anode. Thus, designing strategies that  
8 can promote the AEM mechanism were proposed. However, the elucidated mechanisms  
9 of the CER indicated that the relationship between the key intermediates of the CER  
10 pathway and the AEM pathway of the OER are linearly correlated. The need to dissect  
11 the rate determining step of the preferred pathway is crucial to stabilize transition states  
12 to select for the preferred intermediate. This feat could be accomplished perhaps through  
13 the development of descriptors that moreover incorporate stability parameters to derive  
14 a catalyst at the apex of the volcano curve possessing realistic potency. Indeed,  
15 predictions of the best catalysts must thus be developed with a robustness that accounts  
16 for the multi-faceted complexity involved in heterogeneous electrocatalysis to devise the  
17 most effective system. Overcoming the inherent linear correlations that the proposed AEM  
18 pathway of the OER are subjected to is another potential though challenging means of  
19 achieving selectivity. The water and chloride reagents were moreover shown to  
20 competitively adsorb onto the electrocatalyst surface; the concentration discrepancy  
21 between the water and chloride reagents in solution can thus influence the observed  
22 evolved gaseous product.

23 Achieving selectivity at the anode is therefore a formidable challenge. Design strategies  
24 that modulate the structure of the electrocatalyst such as optimizing the exposure of the  
25 facet with the greatest OER selectivity, introducing point defects in the local chemical  
26 environment, and improving the active site density are ongoing. Indeed, further  
27 implementing the design of correlated single atom catalysts could afford the structural  
28 flexibility to manipulate the type of atom and its proportion within the first and second  
29 coordination shell and optimize the electronic state of the active site to promote selective  
30 adsorbate binding. Ruthenium and its modulable redox state greatly diversifies the  
31 potential coordination environments and the relative energies of its d-band centers,  
32 enabling the optimization of the adsorbate binding. The design of catalysts with greater  
33 conductivities may further decrease the observed OER overpotentials. The most  
34 realizable solution may indeed be the incorporation of an overlayer that arrests the  
35 transport of the chloride ion and decreases its concentration at the active site. Moreover,  
36 development of heterogeneous electrocatalytic systems with a penchant for self-healing  
37 would facilitate the needed stability under the harsh acidic conditions within PEMWE.  
38 Further insights into the effects of the electrified double layer, and the structural sensitivity  
39 of adsorbate binding on the electrocatalysis of the evolved gaseous products may further  
40 the efforts to achieve selectivity for the OER at the anode under the perilous acidic  
41 conditions. Indeed, these design strategies may provide insights into future research  
42 efforts to uncover an optimal electrocatalytic surface for selective OER evolution and  
43 reveal an effective solution as serendipitous as the abundance of a natural resource that  
44 calls to be implemented into our burgeoning societies for the advancement of our future  
45 generations.

46

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