Linking Structure to Function: The Search for Active Sites in Non-Platinum Group Metal Oxygen Reduction Reaction Catalysts

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Abstract: Atomic-scale structures of oxygen reduction reaction (ORR) active sites in non-platinum group metal (non-PGM) catalysts, made from pyrolysis of carbon, nitrogen, and transition-metal (TM) precursors have been the subject of continuing discussion in the fuel cell electrocatalysis research community. Quantum chemical modeling is one path forward for understanding of these materials and how they catalyze the ORR. We here demonstrate through literature examples of how such modeling can be used to better understand non-PGM ORR active site relative stability and activity and how such efforts can also aid in the interpretation of experimental signatures produced by these materials.

TOC Figure:

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Background

The use of non-platinumgroup metal (non-PGM) catalysts for the oxygen reduction reaction (ORR) that occurs at the cathode of proton exchange fuel cells (PEFCs) is not tied to the availability of a scarce commodity as it is for Pt-based catalysts. Non-PGM catalyst materials, based on precursors of Earth-abundant elements of carbon (C), nitrogen (N), and transition metals (TMs), have undergone several dramatic shifts in how they are synthesized, leading to drastically improved ORR activity and durability under fuel cell conditions[1-7]. Despite the improvements, these two catalyst properties, as well as cost of synthesis and reaction selectivity, need even further optimization for non-PGM catalysts to be commercially relevant replacements for Pt-based PEFC cathode materials.

At the heart of improving non-PGM catalysts lies the mystery of the atomic-scale structures of active sites. Due to the pyrolysis of precursor materials in state-of-the-art non-PGM materials synthesis, a wide variety of structures are formed and understanding which component of the material is responsible for ORR activity is still debated. There is still much discussion, in particular, regarding the role of transition metal precursors and whether they are a central component of the active-site structure or whether they are simply required to aid in templating/catalyzing formation of C-N active sites.

This gap in knowledge regarding the fundamental nature of the active site is problematic for a rational approach to catalyst improvement. ORR activity is a function of both active-site density within the material and the turnoverfrequency (TOF) of the sites[4]. Ideally, a material would have a high density of high-TOF sites. Exposure of materials to electrochemical environments may lead to corrosive attack or poisoning of active sites leading to a loss of catalytic activity. As such, active sites should be resistant to corrosion and poisoning in order to maintain high activity under operating conditions for long periods. Knowing how atomic-scale structure couples to both activity and durability could help to guide synthesis to achieve this high density of very active and corrosion-resistant sites.

The last decade has seen acceleration of non-PGM development, as well as the application of quantum chemical calculations for understanding and improving electrocatalysts[8-14]. These calculations can provide valuable insight into electrochemical reaction mechanisms and have matured to the point that prediction of ORR activity as a function of atomic-scale activesite structure is now routine in the literature. In addition to forecasting catalyst activity, these techniques can also be utilized to understand the active-site thermodynamics, which can in turn aid in understanding the probability of given structures being formed and how stable they may be relative to other structures. As the field advances, predictions of mechanism-specific corrosion properties as a function of structure are likely not far off. Quantum chemical calculations can also be useful for trying to de-convolute complicated experimental signatures in pyrolyzed materials and facilitate understanding of the experimental output.

This manuscript contains examples how quantum chemical modeling has been applied to the understanding of non-PGM catalyst materials, with particular attention to linking atomic-scale structures to calculated formation energies, ORR

activities in acidic environments, and experimental signatures. It is not meant as an exhaustive review of available modeling literature but to selectively utilize key publications in order to highlight specific points regarding the importance of atomic-scale structure. It is our hope that this discussion will spur future investigators to consider the use of quantum chemical modeling in their research and to serve as a starting point for such efforts.

1.1 Density Functional Theory

Density functional theory (DFT), when coupled with thermochemical models to form a quantum chemical model, makes for a powerful computational tool for better understanding catalyst properties, including relative stability[15-22], ORR activity[13, 16, 20, 22-29], and selectivity[22, 26, 30, 31]. DFT capabilities are reflected by its increasing use in the field of catalysis. A full description of DFT is beyond the scope of this work but, in brief, DFT solves an approximation of the many-body (electron) Schrödinger equation for an initial guess of atomic structure and returns calculated locally relaxed ground state atomic and electronic structures and relative structure internal energies at 0 K. DFT is well suited to calculations of ~100 atoms and can capture much of the physics important for understanding non-PGM materials at the atomic scale. In particular, formation energies and binding energies are important quantities that can be calculated via DFT. These values can be otherwise difficult to determine accurately at the atomic level for structures on the ~100 atom size scale. Mass-transport contributions to ORR overpotential require larger time- and length-scale approaches[32] and so the relative activities from DFT calculations are limited to the electrode kinetics, represented by the kinetic region in catalyst polarization plots. Despite this limitation, the approach is still invaluable for understanding ORR at the atomic scale and comparing varied atomic-scale structures.

In the approaches discussed below, DFT calculated internal energies are utilized as input for thermochemical models for relative stability and activity. In addition, DFT can be used to obtain vibrational data for calculating zero-point energy (ZPE) and vibrational contributions to entropy. Addition of a solvent and its energetic effects is also possible, though *ab initio* molecular dynamics or addition of a solvation field. Other approaches can add in the effect of double-layer structures generated due to charged surfaces. These approaches attempt to give a more accurate representation of system free energies under *in-situ* conditions. A number of authors have shown, however, that trends in activity can be identified, in most cases without these computationally expensive additions[8, 12, 33]. Further refinements of the thermochemical models and of the DFT values used as input for these models is the focus of many current research efforts.

2. Linking Synthesis Conditions and Structures

Using DFT-calculated energy values for given atomic-scale structures, it is possible to determine formation energies for active site structures *versus* chosen reference states for each of the considered chemical species. These formation energies can be

used to compare the relative stability of active site structures. For instance, if we consider the FeN₄ structure shown in **Figure 1**, there are three chemical species, C, N, and Fe. One choice of reference states is graphene for carbon, molecular N₂ for nitrogen, and bulk body-centered cubic (BCC) Fe for iron. Each of these reference states has a (per atom) reference state energy that can be calculated *via* DFT (E_x , where x is the considered species). These reference states represent the chosen zero point of chemical potential for each of the species. DFT calculation of the FeN₄ structure energy can then be compared to the same number of atoms of a given species at their reference state to give a relative formation energy, $E_{formation}$, given in Equation [1]:

$$E_{formation} = E_{atoms\ in\ structure} - E_{atoms\ in\ reference\ state} \quad [1]$$

For the specific case of the FeN₄ structure in Figure 1, where the Fe occupies a C bivacancy, the N replace 4 neighboring C atoms, and the initial, defect-free graphene structure contains 96 C atoms, the relative formation energy can be calculated as:

$$E_{formation, FeN_4} = E_{FeN_4} + 6E_{C, graphene} - 96E_{C, graphene} - 2E_{N_2} - E_{Fe, bcc} \quad [2]$$

In this example, 6 C atoms are removed from the 96 atom graphene structure to host the Fe and N (2 for the Fe and 4 that are replaced by N atoms) and placed at their reference-state energy. The initial state is defined as the defect-free 96 atom graphene sheet, 2 N₂ molecules (4 N atoms), and 1 Fe atom. If formation energy calculated in this manner is negative, then formation of the defect site is thermodynamically stable *versus* the choice of reference states. By comparing formation energies of different structures, the relative stability is obtained. Assuming a thermodynamic distribution of sites leads to the conclusion that the lower (more negative) the formation energy, the higher the concentration of particular sites. In this way, DFT can be input into a thermochemical formation energy model to compare the likelihood of given sites being present. This approach is agnostic as to the formation pathway and thus ignores any potential kinetic barriers that must be overcome during the synthesis process. Such kinetic barriers are possibly why relatively high pyrolysis temperatures are required in order to achieve highly active catalysts [4].

Through the use of this DFT-based relative stability formalism, the authors have developed three structural motifs governing Fe-N defects in graphene hosts (in the form of either a graphene nanoribbon or a graphene “bulk” sheet) that capture calculated trends in active-site relative formation energies [17-19]:

- 1) Fe substitutional atoms are significantly stabilized by N-coordination. This appears to be true for both three-fold coordination (Fe replacing a single C atom) as well as for four-fold coordination (Fe replacing 2 C atoms).

- 2) Fe-N defects are more stable at the nanoribbon edges vs. central positions. The formation energies at central positions of nanoribbons are slightly lower than those calculated in bulk graphene. Comparing defect formation energies at edges vs. bulk show that for FeN₃ structures, the edge site is ~2.4 eV more stable than bulk (edge structure shown in **Figure 2**) and that for the FeN₄ structure, the edge site is ~1.6 eV more stable than bulk for the chosen reference states. This difference is likely due to the increased perturbation associated with an Fe at a C monovacancy (FeN₃) (also considered by Kabir *et al.* [20]) and the increased ability of the edge to relax this larger perturbation. A similar stabilization effect has been reported for Fe-N defects near pore structures[16, 27], again, likely due to the ability of the local C structure to relax near open edges.
- 3) There is a thermodynamic driving force for edge FeN_x defects to form small clusters[19]. For the FeN₃, there is a particularly strong thermodynamic difference, when Fe atoms are at second nearest neighbor positions with a bridging/shared N. The driving force is less strong for the in-plane FeN₄ structures. Such closely clustered metal sites are likely to have dramatically different ORR behavior compared to single metal atom sites. Multi-metal atom sites are also more likely to experience significant kinetic formation limitations due to the increased structural complexity and the need to have multiple local metal atoms present to form such structures. For Fe and Co, a thermodynamic alloying effect has been demonstrated indicating that combination of Fe and Co is energetically favorable versus formation of segregated structures[24].

Deviations from chosen reference states can be treated as a change in the chemical potential of a given species and entered into Equations [1] and [2] via altered E_x values. The chosen reference state can act as a zero(reference) value for chemical potential and the above formation energy model can be modified to include shifts in chemical potential from this state. As an example, the N₂ molecule reference state could be altered by temperature-dependent contributions to more accurately capture temperature dependencies on formation, changes in N₂ partial pressure to capture environmental effects, or use of a higher energy NH₃ reference state to simulate more directly certain pyrolysis approaches. These changes can be included by a shift in the reference state for N species. (Quantitative values for such energy shifts are often available via tabulated chemical data or via thermodynamic calculation, which can give a range of relevant chemical potential shifts or be utilized to refine reference state values. Such shifts can also be utilized to capture thermodynamic properties of states beyond calculated internal energies.) Changes in reference state can affect the calculated relative stability of structures with differing amounts of a given species, such as N. By including this as a shift in chemical potential, Holby *et al.* determined that there are a variety of stable Fe-N-C structures possible in a zig-zag nanoribbon host C-structure (**Figure 3**) and that which structure has the highest relative stability (represented by the lowest formation energy at a given chemical potential) is a function of both N and Fe

chemical potentials[19]. This indicates that choice of precursor and processing conditions can alter the thermodynamically most stable Fe-N-C structure, allowing for some tunability of synthesized active sites.

DFT-based formation energies also enable thermodynamic comparisons of the predominance of active-site structures. For instance, structural motif in item 2 above, points toward similar structures being more stable at graphene edges vs. bulk. With calculated formation energies, simple assumptions, and application of a Gibbs Measure to describe distribution probability, an estimation of the relative ratio of edge-to-bulk FeN_x structures can be determined. If we assume that there are only two states (edge and bulk) and the probability, P , of each state is given by a canonical partitioning weighted by the concentration of host sites (c_{edge} for edge C and c_{bulk} for bulk C), then, the ratio of edge to bulk sites should be given by Equation [3]:

$$\frac{P_{edge}}{P_{bulk}} = \frac{c_{edge}}{c_{bulk}} \frac{\exp\left[\frac{-E_{formation,edge}}{k_B T}\right]}{\exp\left[\frac{-E_{formation,bulk}}{k_B T}\right]} \quad [3]$$

In this equation, $E_{formation}$ represents the relative calculated formation energies, k_B is the Boltzmann constant, and T is the temperature in Kelvin. If we consider the FeN₃ case and use bulk formation energy as a reference value of zero and a formation temperature, T , of 1173 K (900°C, a common pyrolysis temperature), for there to be an even distribution of edge and bulk sites, the ratio of bulk to edge host sites (c_{bulk}/c_{edge}) must be of the order 10^{10} . For FeN₄, the ratio is of the order 10^6 , still a large number. Even for this lower value, if we assume a zig-zag ribbon geometry composed of only edge and bulk sites (2 edge sites and l bulk sites where l is given by the ribbon width, d , and linear C density, r , such that $l \sim d \times r$), to match such a ratio, the ribbon would need to be hundreds of microns thick ($d \sim 0.5$ mm for $r = 1 \text{ C} / \sim 1 \text{ Å}$) to satisfy such a site ratio. Such a large width is unrealistic for a high surface area carbon with typical lengths on the nanometer scale, thus indicating the likely predominance of edge structures (assuming a thermodynamic distribution). Edge sites are expected to have a kinetic advantage in formation as well, since they are more accessible to Fe and N reactants during synthesis. This simple thermodynamic model, enabled by DFT calculations, highlights the dramatic difference in site concentrations required for an equal thermodynamic distribution between states, heavily favoring defect formation at edges. It also demonstrates the type of data-driven considerations that will aid in understanding the atomic nature of non-PGM ORR active sites.

Another useful approach for considering structural stability is discussed by Kwak *et al.* [20], who utilized a binary alloy approach for understanding relative stability of C-N structures in both bulk and zig-zag nanoribbon structures. There has

been an ongoing debate regarding the effect of N concentration and speciation of C-N structures on ORR catalyst activity, particularly in the context of metal-free ORR active sites. Through DFT-calculated formation energies of over 700 bulk N-doped graphene structures and over 100 edge N-doped graphene nanoribbon structures, Kwak *et al.* [20] developed a convex hull model, showing relative thermodynamic stability of phases as a function of N-doping concentration. For bulk N-doped graphene structures, a specific ordering of N at a fractional concentration of 27.8 at.% N was found to be a formation energy minima and concentration values above this are likely to phase-segregate between this 27.8 at.% N phase and the chosen end-point for more highly N-doped systems (**Figure 4**). At lower concentrations, a variety of C-N phases were found to be on the calculated convex hull including a 5.5 at.% N phase, 11.1 at.% N phase, 16.7 at.% N phase, and a 22.2 at.% N phase. Thus, the predicted thermodynamic phase is strongly dependent upon the N concentration. N concentrations between these phases should phase-segregate to the two neighboring phases following a lever rule, however, due to the coarse graining of N-concentrations required by finite sized calculation cells, it is possible that other intermediate phases exist along the convex hull. Based on literature values of intercalated N concentrations, two of the determined phases are of particular interest, one occurring at 5.5 at.% N and one at 11.1 at.% N. These phases show a lack of N-clustering with the closest N-N distance being at third nearest-neighbor positions (11.1 at.% N). This finding has implications regarding the nature of metal-free (only C- and N-based) bulk ORR active-site structures for materials since this prediction of separated N is likely to affect O₂ binding energies as discussed in the activity section.

For the considered zig-zag nanoribbon structure in Kwak *et al.* [20], the minimum formation-energy phase occurs for N occupying all of the edge positions of the ribbon. For their chosen ribbon, this is a 33.3 at.% N doping but further calculations are required to determine if this edge behavior dominates for thicker ribbons. If the trend of N replacing only edge C atoms would hold, then this would occur at N doping concentrations well below the determined 33.3 at.% level reported in this study for thicker ribbons (with more non-edge C). For instance, edge occupation of an 8 C pair thick ribbon, an edge-only N occupation structure would be 12.5 at.% N. This finding also has implications for the nature of ORR active-site structures, in particular that edge occupation by N is strongly favored vs. more bulk-like positions, an effect that is likely to enhance formation probability of edge-based N-containing structures. Other researchers have considered active-site structures with N at positions other than the position predicted by this work. Such states are meta-stable to the structures reported by Kwak *et al.* [20] and thus are thermodynamically less likely to be formed.

Convex hull calculations as well as formation energy values as a function of chemical potential based on DFT calculations give insight into which structures are thermodynamically favored to form as a function of varied environments. As such, these studies provide useful starting points for determining which atomic-scale structures should be considered for ORR active-site candidates. High-throughput calculations of formation energies can be used to down-select structures for ORR activity calculation and may aid in determining new structures not previously

considered for active-site structures. An important distinction must be made, however, between calculated relative stability between phases and the durability of active sites. While the relative stability can dictate the thermodynamic probability of given structures occurring in the synthesized material, the durability is dependent upon the specific corrosion mechanism that leads to loss of active-site structures in the relevant environment. For instance, edge sites have been shown to have a significantly lower formation energy than their bulk analogs. Edges, however, may be more susceptible to corrosion of the C support and thus edge sites may be more prone to corrosion and deactivation. More research into the corrosion mechanisms behind the loss of ORR active sites and of the effects of active site structure on durability[34] is required to couple DFT-based studies to non-PGM catalyst long-term durability.

3. Linking ORR Activity and Structures

One of the keys to improving non-PGM catalysts is increasing the site density of the most ORR-active structures since total activity is a function of both number of active sites and the turnover frequency (TOF) of those sites. Understanding what active-site structures lead to high ORR activity and high TOF would greatly aid in the pursuit of creation of more active materials, providing target structures for synthesis. In this section, we will discuss how DFT modeling has been applied to understand the ORR reaction in acidic environments and how active-site structure (particularly local C structure, as well as N-doping and speciation) couples to activity.

For over a decade, DFT studies of ORR activity have been used to help guide synthesis of catalyst materials. This is due largely to the success of the computational hydrogen electrode (CHE) thermochemical model, described by Norskov, *et al.*[8] and other models that produce a DFT-accessible descriptor of ORR activity. In this methodology, DFT is used to calculate binding energies of ORR intermediates on active-site structures. These binding energies, as well as carefully chosen reference states, give energy values to chosen sub-steps of the ORR reaction (for example, those given by Equation[4a-e]), as well as the system energy dependence on potential. Combining these system energies provides a calculated thermodynamic reaction pathway as a function of potential, which is added post-calculation as part of the CHE thermochemical model. This approach enables calculation of the thermodynamic limiting potential, U_l , above which there is a thermodynamic barrier between two or more states. In addition, the potential-determining step, the reaction that sets the limiting potential, can also be calculated in this formalism. The value of U_l can serve as a DFT-accessible descriptor of ORR activity and when coupled with the potential-determining step is useful for uncovering trends in activity as a function of atomic-scale structure. Examples of these quantities and their more detailed description are given in the next section.

While ignoring kinetic barriers between thermodynamic states and non-local electronic / chemical effects, this approach enables a direct comparison of predicted ORR activities as a function of active-site atomic-scale structure for a given reaction pathway. Additionally, different reaction pathways can be tested to determine if, for

example, an associative vs. dissociative mechanism is likely to occur in the ORR or if H_2O_2 is thermodynamically likely to be formed, which would affect catalyst selectivity. This approach has been widely utilized in understanding how metal and metal alloy surfaces can be tuned to improve ORR activity but researchers have also utilized this method for understanding the activity of proposed non-PGM active-site structures. This approach is particularly useful for considering the role of transition metals in the active-site structure. An example of how this approach can be utilized, followed by literature examples of ORR activity calculations for both metal-bearing and metal-free structures, are given in this section.

CHE Methodology Example

The CHE methodology enables charge-neutral DFT calculations to be used to approximate the effects of electric potential on electrochemical reaction pathways. Detailed discussions are available in references [8, 12, 14, 23] but this example will serve as a brief introduction to the approach. This example assumes ORR in acidic media following the associative reaction with sub-steps given in Equations [4a-e]:

In these equations, * indicates the active site and *X represents chemical moiety X bound to the active site. This reaction is composed of one initial chemical reaction (O_2 binding to the active site, [4a]) and four subsequent protonation reactions [4b-e], leading to generation of 2 H_2O molecules from one O_2 molecule, 4 protons, and 4 electrons. To apply the CHE, several assumptions are made. The final state containing the active site (E^*) and 2 H_2O molecules ($2 E_{H_2O}$) is taken to be 0 eV to set the energy scale. The energy of this state is calculated by adding the calculated energies of the active site, *, with the energies of 2 H_2O molecules. The initial state is assumed to be 4.92 eV higher than the final state at standard conditions, based on the known thermodynamics of the ORR and consistent with a standard redox potential of 1.23 V vs. SHE for the 4 electron reaction [7]. To set the electric potential, an assumption is made that at a potential of 0 V ($U = 0$ V), that two protons and two electrons are degenerate in energy to an H_2 molecule at a pH of zero. This assumption is analogous to the experimental use of a hydrogen-based reference electrode, leading to the term computational hydrogen electrode. The contribution to system energy of the protons and electrons at each sub-step as a function of electric potential is thus accessible via calculation of the H_2 molecule. If a non-zero potential is considered, then the system energy is decreased by the considered potential, multiplied by the number of electrons at that state. Hence, higher

potentials stabilize states with electrons and at a potential of 1.23 V (and standard conditions), the initial and final states are in thermodynamic equilibrium. In an ideal pathway, all considered states are in equilibrium, leading to no thermodynamic barriers up to 1.23 V vs. CHE. Many studies have focused on acidic environments where fuel cell membrane technology is most mature. Reaction pathways and, subsequently, relative ORR activities, are likely to be different in basic environments. This difference is exemplified by the relatively high ORR activity of Pt in acidic environments but relatively moderate activity in basic environments.

For the above assumed reaction pathway, calculation of the H_2 molecule state, H_2O molecule state, the active-site structure $*$, the $*OO$ bound structure, the $*OOH$ bound structure, the $*O$ bound structure, and the $*OH$ bound structure are required. The initial and final states are fixed (for standard conditions), as discussed. For the other sub-step states, a system energy relative to the final energy is calculated. For instance, for the second sub-step that contains the $*OO$ structure, 4 protons, and 4 electrons, DFT is used to calculate the energy of the $*OO$ bound structure (E_{*OO}) and the energy of 2 H_2 molecules is added to take into account the 4 protons and electrons. The calculated system energy for the final state is then subtracted off giving the relative reaction energy for the second sub-step. Similarly, the $*OOH$, $*O$, and $*OH$ bound structures, along with the appropriate contribution to system energy from the H_2 and H_2O , can be used to obtain the relative reaction energy for reaction coordinates 3, 4, and 5. These relative reaction energies represent the reaction pathway at $U = 0$ V.

Since the number of electrons at each state is known for the assumed pathway, a shift in potential can be applied after the calculations. There is an implicit assumption in this method that ORR intermediate binding energy is not directly affected by this shift in potential and that the dominant effect is due to the electrons present at each of the sub-steps. In this formalism, there is some applied potential, at which two of the sub-steps will be degenerate and, due to the decreasing number of electrons at increasing reaction coordinate (sub-steps farther along the reaction pathway), above this potential, there will always be at least one (and possibly multiple) thermodynamic barrier between the sub-steps. This value is called the limiting potential, U_l , as described above and can serve as a DFT-accessible descriptor of ORR activity. Structures with higher calculated U_l values do not have thermodynamic barriers in their reaction pathways until subjected to higher potentials as compared to structures with lower U_l values, and are therefore predicted to have higher activities. Correspondingly, at a fixed potential above the U_l value of two sites, the thermodynamic barrier in the ORR reaction pathway is smaller for the site with the higher U_l value and larger for the site with the lower U_l value. The reaction that becomes degenerate at the limiting potential is called the potential-determining step and is important for understanding what is limiting the ORR. General trends based on limiting potentials and their potential-determining steps can be drawn. Further interrelations between sub-steps, known as scaling laws, have been demonstrated but are beyond the scope of the present work.

Clearly, this approach contains a multitude of approximations, as does any model attempting to capture complex behavior, but provides a computationally accessible method for linking active-site structures to ORR activity for comparison

purposes. Other reaction pathways can be considered through variations in calculated sub-states. Deviations from ideal and standard conditions can also be introduced. Sensitivity to model choices/assumptions can be explored and a more uniform methodology, enabling comparison between calculations of different research groups, are all possible due to this useful computational approach.

3.1 Metal-Bearing Active Sites

Active-site structures considered in literature can be broken down into sites that contain transition metals (metal-bearing) and those that do not (metal-free). It is well documented that materials synthesized with metal precursors lead to significantly more active ORR catalysts[35] but it is possible that either the metal itself is a central part of the active site or acts to catalyze/template formation of specific ORR active C-N structures. This distinction is made more complicated due to trace amounts of transition metals present in many “metal-free” materials, as discussed by Wang *et al.*[36]. Another complication arises when a two-site ORR reaction occurs, in which one site generates H_2O_2 that is further reduced to two water molecules on a secondary site[37]. In contrast to “4 e⁻ pathways”, this “2+2 e⁻ pathway” is likely to generate significantly more H_2O_2 , which may degrade fuel cell polymer membranes. DFT can be useful for determining which pathway is thermodynamically favored and thus gives clues to the selectivity of a given active-site structure toward preferable 4 e⁻ pathways[14].

Even if such complications are avoided and a single active site following a given 4 e⁻ pathway with a transition metal(TM) as the ORR intermediate adsorption site is assumed, a variety of structural questions still remain. How does N-coordination of TM affect activity? How does local carbon-support structure affect activity? Which transition metals make the best ORR catalysts? In general, what is the optimum TM-N-C active-site structure and how can this knowledge be used to synthesize better non-PGM catalyst materials? While many of these questions remain unanswered, we will discuss here some of the progress that has been reported using DFT to better understand how TM-N-C structure couples to ORR activity.

Calle-Vallejo *et al.*[13] report calculations of ORR via a 4e⁻ associative pathway with no initial chemical adsorption of O_2 on two M-N₄ bulk graphene structures with varied metal (M) species (including non-transition-metals, M = Cr, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au). The first structure (Cell A) contained 5 member rings coordinating M and the second structure (Cell B) places M at the center of an N-coordinated C divacancy (analogous to the FeN₄ structure discussed previously in the Stability section). These structures are shown in **Figure 5**. Mn, Fe, and Co M-species were calculated to be the most ORR-active M-N₄ sites. Cell B was reported to be more active than Cell A for Co and Cell A more active for Mn and Fe. These findings highlight the sensitivity of ORR activity to transition metal species, as well as to local carbon structure, as represented by the two different cell structures.

Kattelet *et al.*[25] demonstrated that other transition metal species may have alternate active structures, as compared to the more canonical graphitic (embedded) M-N₄ sites. They considered the activities of a Ni-N₄ graphene bulk

system, as well as a Ni-N₂ nanoribbon armchair edge structure, with the Ni adsorbed at an edge, and reported that the edge structure is a more likely candidate for the ORR active site in acidic media, based on calculated activity. The same authors also considered how N-coordination of graphene-embedded Co affects ORR activity and selectivity[26]. Based on stability constraints from DFT calculated formation energies, a 4-fold N-coordination is thermodynamically likely but this structure is predicted to preferentially generate H₂O₂, requiring a second active site for the 2+2 e⁻ ORR reaction. These studies again highlight the importance of atomic-scale structure, including N-coordination, on ORR activity and add the consideration that active sites at or near edges may behave differently than those contained in the bulk of the graphene structure.

A correlation between ORR activity and porosity of materials has been identified experimentally[3, 4], prompting two groups to consider the formation and activity of TM-N₄ structures in and near models of such pores. Kattel and Wang[27] reported that, similarly to the stabilization of defects near edges discussed above, TM-N₄ defects are structurally stabilized in pore-like structures compared to bulk graphene. Szakacs *et al.*[16] also suggest that, unlike graphene bulk structures that predominantly contain flat Fe-N₄ defects, pore-supported defects may distort out of plane, altering the local structure. Such defects, when incorporated into bulk graphene, are found to be flat/planar to the graphene host. Both groups consider O₂ binding as a function of structure and determine that the final protonation step from *OH to H₂O is likely the potential-determining step in such structures. Szakacs *et al.* also consider the idea of a ligand modification of the Fe-N₄ pore site and its effect on calculated ORR, an idea proposed by Zhu *et al.*[38] for shifting O₂ binding energies in non-PGM active sites. They determine that this ligand can alter the reaction pathway. This suggests that understanding of ligand interaction/modification of active sites may be a valuable tool in optimizing stability, ORR activity, and selectivity.

Following previous studies considering structural stability, Holby and Taylor calculated ORR activity on an Fe₂N₅ zig-zag edge structure (Figure 6), finding that a strongly bound *OH in the ORR reaction pathway is likely to be persistent at relevant potentials[24]. Similar to the works of Zhu *et al.* and Szakacs *et al.*, this *OH was treated as a modifying ligand, albeit one that is calculated to form spontaneously during ORR. The spontaneous *OH ligand modification dramatically improved the ORR activity on the Fe₂N₅ site, which, due to its 3-dimensional nature, was not blocked by the bound *OH as would occur on 2-dimensional metal surfaces. Applying this ligand effect to a mixed-metal FeCoN₅ zig-zag edge structure produced an active site with a predicted *U*_V value of 0.80 V, the highest calculated ORR activity for non-PGM structures that includes the chemical adsorption of O₂. This effect has also been calculated to apply to a variety of TM-N₄ edge structures and is likely a general effect for non-PGM active sites, in which the potential-determining step is the final protonation.

Another active-site structure, suggested based on thermodynamic stability, is the Fe₂N₆ structure (Figure 7)[19]. Unlike many other TM-bearing sites, this structure's calculated potential-determining step is the first protonation reaction due to the strong O₂ binding. Owing to the more weakly bound *OH moiety,

spontaneous *OH ligand modification is not predicted to occur on such structures at potentials below calculated limiting potentials. When hosted at a zig-zag edge, the limiting potential is calculated to be 0.37 V. Compared to the Fe₂N₅ structure, the Fe₂N₆ structure is less strongly stabilized by proximity to an edge, which is attributed to decreased strain for the 4-fold N coordinated structures that make up this site. The limiting potential for the graphene-bulk-hosted structure is slightly improved with a calculated value of 0.42 V. If, for the sake of argument, the initial O₂ adsorption and first protonation step are combined into a single electrochemical reaction step, the calculated limiting potentials would be drastically increased to 0.91 V and 0.98 V for the zig-zag and bulk structures, respectively. This assumption is often made in literature (as will be discussed below) and is still a matter of debate. Such a dramatic difference in calculated activity in these two cases could be utilized to experimentally determine if an initial chemical step does occur (assuming it would be possible to synthesize such structures homogeneously).

It is clear that a diversity of active-site structures involving TMs may be formed during synthesis and, based on DFT calculations, these structures are likely to have widely varying ORR activity. N-coordination, planarity, position in relation to edge/pores, and modifying ligands have all been identified as potentially important contributors for linking ORR activity to metal-bearing active-site structures.

3.2 Metal-Free Active Sites

Even if transition metal precursors are required for synthesis of highly active non-PGM materials, that does not directly indicate that these metal atoms are at the center of active sites, as discussed in the previous section. While such sites can have quite high calculated ORR activity, that does not preclude other active sites that do not include TMs. TM atoms have been reported to catalyze formation of C vacancies[39], which may aid in doping of N or form more complex defect reconstructed structures, which in turn may possess high catalytic activity[29]. Formation of persistent TM-rich nanoparticles (possibly carbides, oxides, sulfides, nitrides, or metal), surrounded by protective carbon layers, have been observed in synthesized materials and some authors have suggested that this may template ORR active sites on the C surface[40-42] or alter ORR activity of N-doped graphene[43]. Other groups, however, have synthesized materials without transition metal nanoparticle formation and without loss of high activity[44], suggesting this effect is not necessarily responsible for high ORR activity. Additionally, at least one DFT study [43] considering N-doped C layers over a metal substrate determined a limiting potential similar to that reported for metal-free N-doped graphene [22], both significantly below the high limiting potentials calculated for metal-bearing sites discussed in section 3.1. Given that TM nanoparticles compete for TM precursor atoms during synthesis and do not lead to improved activity, future work should focus on synthesis routes that avoid formation of such nanoparticles.

Without assuming what role the transition metal atoms play in formation of active sites, a variety of truly metal-free structures have been suggested and their activity explored using DFT. Generally speaking, metal-free sites tend to bind ORR intermediates less strongly than metal-bearing sites, in many cases leading to the

first protonation step being potential determining. In fact, for many C-N structures, O₂ does not exothermically bind but, instead, has been found to occupy a locally meta-stable position above the active site[29, 45]. Due to this effect, a reaction pathway similar to that in Equations [4a-e], but with the first two sub-reactions combined into a single binding/electron transfer step, is often assumed, leaving 4 electrochemical sub-reactions in the 4e⁻ pathway (and no initial chemical step). In this new pathway, Equations [4a] and [4b] are replaced by Equation 5. If this assumption were not made, there would either be a thermodynamic barrier in the reaction pathway for all potentials due to the O₂ meta-stability or, the reported limiting potentials would be incorrect since the first electrochemical step would be between the bound *OO state and the *OOH state, not the O_{2(g)} state and the *OOH state. Since the first protonation step is often the potential determining step for metal-free sites, the calculation of the limiting potential is particularly sensitive to this choice. The validity of this assumption remains one of the outstanding considerations in the field of ORR active-site modeling. Because of this, particular attention is paid to consideration of O₂-active site interactions when studying metal-free active-site structures. With the caveat of this assumption made, we present examples of metal-free active-site structures and DFT findings on how structure couples to ORR activity and attempt to provide details of the O₂-active site interaction, where available. Generally, based on comparisons of OOH binding energies, the C adjacent to doped-N is found to serve as the intermediate binding site similar to the metal atom in the metal-bearing structures.

Okamoto used first-principles molecular dynamics based on DFT to study ORR on N-doped graphene structures[46]. In this work, it was determined that increased N-doping leads to increased O₂ binding and that doping values above 9 at.% N (3 and 4 N atoms in their 32 C unit cell) were required for O₂ to adsorb exothermically. Furthermore, high N-content structures were comprised of second nearest-neighbor N clusters, which were shown by Kwak *et al.*[20] to be not representative of stable C-N phases, up to 11.1 at.% N. Thus, such structures would only be kinetically stable. Using a different electrochemical model for ORR activity via an associative pathway, Okamoto predicted that these highly N-doped materials are likely to have minimum reversible potentials (analogous to *U*) of 0.34 V for bulk and 0.39 V for edges with protonation of adsorbed *O being the limiting step in the considered water environment. These findings highlight one of the central issues faced by metal-free active sites: structures that bind O₂ exothermically are rare and do not appear to have very ideal reaction pathways.

Kim *et al.* also considered ORR on N-doped graphene structures and proposed a novel ring-opening pathway, in which the adsorbed *OOH cleaves a C-N bond near zig-zag edges[28]. This pathway shifts the minimum reversible potential step, creating a more favorable ORR pathway. The considered N-doping site, however, is not consistent with calculated thermodynamically favorable N doping positions of such edges and the stable structures (with N occupying the outermost C of the zig-

zag edge) were not tested. The proposed ring-opening reaction pathway was reported by Kwak *et al.*[20] for highly N-doped (~ 27.8 at.% N) edge structures that are consistent with N at the outer zig-zag edge but the authors considered the structure susceptible to degradation and did not report limiting potential values for this structure.

In addition to this high N-doping zig-zag structure, Kwak *et al.* considered lower N-doping of graphene sheets and zig-zag edged nanoribbons. These structures all fall on the calculated thermodynamic convex hull and thus represent the thermodynamically predicted structures for N-doped bulk and zig-zag edge nanoribbons. The authors reported that bulk structures are more ORR-active than edge structures due to stronger $\ast\text{O}$ binding at edges. For bulk graphene structures, they reported a very strong dependence of limiting potential on N-doping and that in general, the lower the N-doping, the more active the material (higher U_l). A recent review of experimental data of synthesized (metal-bearing) materials with the highest ORR mass activity showed no significant trend relating N-content to activity but significantly lower N-doping levels (up to ~ 4 at.% N) were reported[4]. This indicates that perhaps this trend only occurs for more highly N-doped materials and also suggests that further increasing of N-doping concentrations is not ideal for improving ORR activity.

Changes in reaction pathways with the addition of solvation effects are shown by Kwak *et al.*[20] to have a large impact on reported limiting potentials, as the solvation stabilizes $\ast\text{OOH}$ binding (or $\ast\text{O} + \text{OH}$ binding) which is integral to their potential determining step. Disregarding a chemical $\ast\text{OO}$ adsorption step, they found a maximum limiting potential of 0.79 V for solvated 5.5 at.% N-doped graphene structures. The same structure without solvation effects was calculated to have a limiting potential of 0.55 V. This value is very close to the value reported by Studt, who reported a limiting potential of 0.51 V on a 6.3 at.% N-doped graphene sheet without solvation effects[23]. The stated potential determining step, however, differs between these two studies with Kwak *et al.* reporting the first protonation step to be potential determining and Studt reporting the protonation of $\ast\text{O}$ to be potential determining (third protonation step). There are several reasons that may explain these variations (underlying choices of DFT, different N-doped structures, etc.) but the possibility of solvation environment affecting reported limiting potentials is an important consideration.

Lyalin *et al.* considered the concurrent contributions of solvation, zero-point energy, and vibrational entropy on binding energies of ORR intermediates on B-N structures and found that for most intermediates (with the exception of a $\ast\text{O} + \ast\text{OH}$ state), these effects largely cancelled each other out[33]. This finding is consistent with Anderson, who reported that using uncorrected DFT calculated gas-phase binding from internal energy values for determining free energies of intermediate states (no zero-point energy, no entropic effects, no solvation effects, and no charge/double layer effects) produced at most a 0.2 V error in calculation of reversible potentials[12]. Further work, particularly closely linked theoretical and experimental studies on well-defined systems, will greatly aid in understanding what role both N-content and solvation environment play in determining ORR

activity and what modifications DFT-based models may require to capture these effects.

Formation of C vacancies and associated defects may be one way in which transition metal atoms aid in formation of active sites without being a part of the active site itself. Chai *et al.* considered ORR activity for a host of N-doped graphene, graphene edge and nanotube structures with and without relaxed C-vacancy structures, including Stone-Wales (SW) defects. They found that defects could significantly alter O_2 interaction with the surface but that for all considered sites, O_2 did not bind exothermically but rather occupied a meta-stable site above the surface. Thus, the direct protonation of $O_{2(g)}$ to form $*OOH$ was considered without the initial chemical adsorption of $O_{2(g)}$. Consideration of relative stability *via* a calculated convex hull as a function of N-doping of a SW defect in graphene indicated that a doping level of ~ 3.3 at% N (with N in well-defined positions in relation to the defect) was thermodynamically most favorable, with lower and higher doping levels being less thermodynamically stable. For bulk graphene, this site had a calculated limiting potential of 0.55 V, similar to N-doped graphene in other studies. Graphene structures with multiple N in the neighboring carbon ring were found to have a lower limiting potential of ~ 0.32 V, suggesting a deleterious effect of additional local N on activity, as also suggested by Kwak *et al.* [20] in their study of N-doped graphene.

Chai *et al.* also considered the effect of curvature on limiting potential [29]. They discovered through the simulation of nanotubes of different radii that curvature (and likely induced strain that it causes) could be used to tune binding energy and thus alter the calculated limiting potential value since the potential determining step was sensitive to choice of radius. They found that by embedding their most stable SW defect with 2N in a (10,0) nanotube that the limiting potential, calculated without intermediate O_2 binding, could be increased to 0.80 V. Their data demonstrates a “volcano plot” for activity as a function of nanotube radius, exemplifying the Sabatier principle in which nanotube radius controls relative binding and shifts from overbinding to underbinding with some peak, activity maximizing value. The strain-engineering of catalysts has been previously applied to other systems [47] and holds great promise for increasing the ORR activity of non-PGM catalysts.

Similar to metal-bearing non-PGM sites, metal-free site ORR activities are clearly dependent upon not only N-doping concentrations but also local C-N configurations. While the issue of the binding of O_2 to such sites remains, even for optimized N-doped structures, C-defect and strain-engineering are demonstrated to be useful tools for tuning ORR activity and, along with the approaches discussed in the metal-bearing catalyst section, will provide useful pathways for improving the ORR activity of synthesized non-PGM ORR materials.

4. Linking Experimental Signatures and Structures

The previous sections discuss how DFT is utilized in a bottom-up approach to determine the atomic-scale nature of sites that are both stable relative to other active-site candidates and highly ORR active. With enhanced understanding of such

sites, it is possible for DFT modeling to help guide synthesis efforts in order to maximize the number of such sites in real, synthesized materials. However, this connection between desired active site and realized active site from synthesis can be difficult to make. As a variety of increasingly active and durable catalysts are being synthesized, it is also possible to utilize DFT in a top-down approach in order to better understand the relationship between the experimental signatures produced by these ORR-active synthesized materials and the atomic-scale nature of the active sites that they contain. We briefly discuss studies that utilize this approach in order to demonstrate usefulness of such efforts and how DFT can aid in interpretation of experimental data. It should be pointed out, however, that there is a fundamental hurdle faced universally in the field of catalysis that is particularly pertinent to such studies. High catalytic activity may be due to numerous moderately active sites (which may dominate experimental signatures) or the activity may be dominated by relatively rare sites with exceptionally high catalytic activity (which may not appear dominant in experimental signatures). Thus, it is important to couple trends from a given experimental signature with observed catalytic activity when possible.

The above DFT studies suggest that for metal-bearing active sites, ligand modification may be an important component of explaining ORR activity. Such ligand effects should have experimental signatures. For instance, Szakacs *et al.* suggest that Mössbauer spectroscopy spin-state signatures of highly active synthesized metal-bearing catalyst materials can be explained by a combination of given active sites with and without a 5th axial ligand which DFT calculates to have nearly degenerate formation energies [16]. Jia *et al.* [48] suggest a switching behavior that is accompanied by a decrease in Fe-N bond distance during the ORR reaction as measured by *in-situ* EXAFS for a highly ORR active PANI-Fe-C catalyst. A less active phthalocyanine-based catalyst displayed a lengthening of the Fe-N bond distance under ORR conditions. DFT calculations of FeN₄ with and without NH₂ ligand predicted both an increase in calculated ORR activity with ligand vs. ligand-free structures and a decrease in Fe-N bond length during ORR due to adsorption of intermediates opposite the ligand, pulling the central Fe atom back toward the graphene host plane. Zitolo *et al.* demonstrated that XANES data is best fit by FeN₄ structures, in which multiple O₂ molecules are bound to the Fe site, suggesting the possibility of ligand occupation. Subsequent DFT calculations indicate that O₂ binding energies are sensitive to an initial ligand (in their case, O₂) [44]. This suggests that the ORR pathway may be affected by the presence of ligands that are themselves ORR intermediates, as suggested earlier by Holby and Taylor based on DFT calculations [24]. While the exact chemical nature of active-site ligand modification is still under consideration, a growing amount of both DFT and experimental literature suggest that such an effect appears to be an important aspect of highly ORR-active materials and provides a potential path forward for tuning active sites toward higher ORR activity.

X-ray photoelectron spectroscopy (XPS) represents a valuable tool for identifying the atomic-scale nature of non-PGM active-site structures. However, deconvolution of experimentally derived XPS data depends on fitting to models of binding energy spectra. In some cases, these models have been obtained from

known structural sources but in cases where no such model exists, DFT can be utilized for generation of such a model. Artyushkova *et al.* demonstrated the validity of such an approach to TM-N_x structures, through calculation of the N 1s core electron shifts in comparison to known model structures[49]. Kabiret *al.* applied this approach to several Fe/Co-N₃ structures, showing that their calculated N 1s core level shift is consistent with XPS data from active ORR catalyst materials, thus suggesting the feasibility of such structures as active sites[21].

The above efforts demonstrate how DFT studies can aid in the interpretation of experimental data and relate experimental signatures to atomic-scale structures. Other surface-sensitive approaches are being actively pursued for identification of synthesized ORR catalysts and DFT will almost certainly remain a useful tool for interpreting the signatures generated by these highly heterogeneous materials in experimental studies.

5. Future Directions

The application of DFT modeling is greatly aiding in the effort to understand the atomic-scale structures in pyrolyzed TM-N-C and N-C materials that give rise to very high ORR activities. Active sites with calculated activities rivaling that of Pt have been demonstrated and future studies will aid in further increasing activity, durability, and 4e⁻ pathway selectivity. Models of catalyst corrosion and poisoning mechanisms are required to fully understand how active sites are lost during fuel cell operation. With the increased knowledge of the atomic-scale structures likely being responsible for ORR activity, such models are now within reach. Further understanding of the link between active sites and modifying ligands may provide a path forward for carefully tuning ORR activity and selectivity. Intentional integration of optimized ligand moieties into catalytic materials may enable catalysts even more active than Pt. Improved modeling techniques, combining the diverse variety of physical and chemical phenomena experienced under fuel cell operating conditions may open further possibilities for improved electrocatalysts and aid in settling the now 60 year old conundrum of what are the structures responsible for ORR in TM-N-C materials and how can these structures be further optimized to enable cost-effective fuel cell technology.

Vitae

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Figures

Figure 1: FeN_4 structure with Fe in C bivacancy, N substituting for 4 neighboring C atoms and a periodic graphene sheet structure as viewed from above. Gray spheres represent C, blue spheres represent N, and the bronze sphere represents Fe.

Figure 2. FeN_3 structure at a zig-zag edge with Fe in C vacancy, N substituting for 3 neighboring C atoms and a periodic nanoribbon structure, as viewed from above. Gray spheres represent C, blue spheres represent N, and the bronze sphere represents Fe.

Figure 3: Stability plot of formation energy of different N and Fe/N zig-zag edge nanoribbon structures as a function of N chemical potential at a fixed Fe chemical potential (from reference [19]). GNR is the defect-free nanoribbon and other structures represent chosen C-N and C-N-Fe structures. This plot emphasizes how changes in chemical potential affects which phase is calculated to be most stable (lowest on the plot at a given N chemical potential).

Figure 4: DFT-calculated convex hull of N-doped graphene (from reference [20]). Such studies provide thermodynamic insight regarding relative stability of atomic arrangements. Of particular interest from this study is the finding that N-doped atoms do not prefer neighboring positions.

Figure 5: Two different implementations of M-N₄ structures utilized in reference [13]. Changes in the local C environment were found to impact relative stability of structures as well as their adsorption characteristics (and thus activity). Changes in central metal atom also had a marked effect on predicted ORR activity.

Figure 6: $\text{Fe}_2\text{N}_5(*\text{OH})$ structure utilized in reference [24]. This and other structures exhibit a spontaneous $*\text{OH}$ ligand modification effect in which a persistent $*\text{OH}$ ligand is likely to be formed at potentials below the calculated limiting potential. This modification modifies ORR intermediate adsorption energies and thus the activity of these sites.

Figure 7: Fe₂N₆ zig-zag and bulk structures. Such structures and their activities may be useful for determining if the chemical adsorption of O₂ is the initial step in the ORR on non-PGM catalysts.

References

- [1] R. Jasinski, *Nature*, 201 (1964) 1212-1213.
- [2] S. Gupta, D. Tryk, I. Bae, W. Aldred, E. Yeager, *Journal of Applied Electrochemistry* 19 (1989) 19-27.
- [3] M. Lefevre, E. Proietti, F. Jaouen, J.-P. Dodelet, *Science* 324 (2009) 71-74.
- [4] F. Jaouen, E. Proietti, M. Lefevre, R. Chenitz, J.-P. Dodelet, G. Wu, H.T. Chung, C.M. Johnston, P. Zelenay, *Energy & Environmental Science* 4 (2011) 114-130.
- [5] G. Wu, K.L. More, C.M. Johnston, P. Zelenay, *Science* 332 (2011) 443-447.
- [6] Z. Chen, D. Higgins, A. Yu, L. Zhang, J. Zhang, *Energy & Environmental Science* 4 (2011) 3167-3192.
- [7] G. Wu, A. Santandreu, W. Kellogg, S. Gupta, O. Ogoke, H. Zhang, H.-L. Wang, L. Dai, *Nano Energy* (present issue).
- [8] J.K. Norskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J.R. Kitchin, T. Bligaard, H. Jonsson, *Journal of Physical Chemistry B* 108 (2004) 17886-17892.
- [9] F. Abild-Pedersen, J. Greeley, F. Studt, J. Rossmeisl, T.R. Munter, P.G. Moses, E. Skulason, T. Bligaard, J.K. Norskov, *Physical Review Letters* 99 (2007) 016105.
- [10] J.K. Norskov, T. Bligaard, J. Rossmeisl, C.H. Christensen, *Nature Chemistry* 1 (2009) 37-46.
- [11] A.B. Anderson, J. Uddin, R. Jinnouchi, *The Journal of Physical Chemistry C* 114 (2010) 14946-14952.
- [12] A.B. Anderson, *Physical Chemistry Chemical Physics* 14 (2012) 1330-1338.
- [13] F. Calle-Vallejo, J.I. Martinez, J. Rossmeisl, *Physical Chemistry Chemical Physics* 13 (2011) 15639-15643.
- [14] I.C. Man, H.-Y. Su, F. Calle-Vallejo, H.A. Hansen, J.I. Martínez, N.G. Inoglu, J. Kitchin, T.F. Jaramillo, J.K. Nørskov, J. Rossmeisl, *ChemCatChem* 3 (2011) 1159-1165.
- [15] S. Kattel, P. Atanassov, B. Kiefer, *The Journal of Physical Chemistry C* 116 (2012) 8161-8166.
- [16] C.E. Szakacs, M. Lefevre, U.I. Kramm, J.-P. Dodelet, F. Vidal, *Physical Chemistry Chemical Physics* 16 (2014) 13654-13661.
- [17] E.F. Holby, C.D. Taylor, *Applied Physics Letters* 101 (2012) 064102.
- [18] E.F. Holby, G. Wu, P. Zelenay, C.D. Taylor, *ECS Transactions* 50 (2012) 1839-1845.
- [19] E.F. Holby, G. Wu, P. Zelenay, C.D. Taylor, *The Journal of Physical Chemistry C* 118 (2014) 14388-14393.
- [20] D. Kwak, A. Khetan, S. Noh, H. Pitsch, B. Han, *ChemCatChem* 6 (2014) 2662-2670.
- [21] S. Kabir, K. Artyushkova, B. Kiefer, P. Atanassov, *Physical Chemistry Chemical Physics* 17 (2015) 17785-17789.
- [22] S. Kattel, P. Atanassov, B. Kiefer, *Physical Chemistry Chemical Physics* 16 (2014) 13800-13806.
- [23] F. Studt, *Catalysis Letters* 143 (2013) 58-60.
- [24] E.F. Holby, C.D. Taylor, *Scientific Reports* 5 (2015).
- [25] S. Kattel, P. Atanassov, B. Kiefer, *The Journal of Physical Chemistry C* 116 (2012) 17378-17383.

- [26] S. Kattel, P. Atanassov, B. Kiefer, *Physical Chemistry Chemical Physics* 15 (2013) 148-153.
- [27] S. Kattel, G. Wang, *Journal of Materials Chemistry A* 1 (2013) 10790-10797.
- [28] H. Kim, K. Lee, S.I. Woo, Y. Jung, *Physical Chemistry Chemical Physics* 13 (2011) 17505-17510.
- [29] G.-L. Chai, Z. Hou, D.-J. Shu, T. Ikeda, K. Terakura, *Journal of the American Chemical Society* 136 (2014) 13629-13640.
- [30] V. Viswanathan, H.A. Hansen, J. Rossmeisl, J.K. Norskov, *The Journal of Physical Chemistry Letters* 3 (2012) 2948-2951.
- [31] T.S. Olson, S. Pylypenko, S. Kattel, P. Atanassov, B. Kiefer, *The Journal of Physical Chemistry C* 114 (2010) 15190-15195.
- [32] L. Chen, G. Wu, E.F. Holby, P. Zelenay, W.-Q. Tao, Q. Kang, *Electrochimica Acta* 158 (2015) 175-186.
- [33] A. Lyalin, A. Nakayama, K. Uosaki, T. Taketsugu, *Physical Chemistry Chemical Physics* 15 (2013) 2809-2820.
- [34] G. Zhang, R. Chenitz, M. Lefevre, S. Sun, J.-P. Dodelet, Nano Energy (present issue).
- [35] G. Wu, P. Zelenay, *Accounts of Chemical Research* 46 (2013) 1878-1889.
- [36] L. Wang, A. Ambrosi, M. Pumera, *Angewandte Chemie International Edition* 52 (2013) 13818-13821.
- [37] K. Artyushkova, A. Serov, S. Rojas-Carbonell, P. Atanassov, *The Journal of Physical Chemistry C* 119 (2015) 25917-25928.
- [38] H. Zhu, S.J. Paddison, T.A. Zawodzinski Jr, *Electrochimica Acta* 101 (2013) 293-300.
- [39] D.W. Boukhvalov, M.I. Katsnelson, *Applied Physics Letters* 95 (2009) 023109.
- [40] D. Deng, L. Yu, X. Chen, G. Wang, L. Jin, X. Pan, J. Deng, G. Sun, X. Bao, *Angewandte Chemie International Edition* 52 (2013) 371-375.
- [41] Y. Hu, J.O. Jensen, W. Zhang, L.N. Cleemann, W. Xing, N.J. Bjerrum, Q. Li, *Angewandte Chemie International Edition* 53 (2014) 3675-3679.
- [42] K. Strickland, E. Miner, Q. Jia, U. Tylus, N. Ramaswamy, W. Liang, M.-T. Sougrati, F. Jaouen, S. Mukerjee, *Nature Communications* 6 (2015).
- [43] S.H. Noh, D.H. Kwak, M.H. Seo, T. Ohsaka, B. Han, *Electrochimica Acta* 140 (2014) 225-231.
- [44] A. Zitolo, V. Goellner, V. Armel, M.-T. Sougrati, T. Mineva, L. Stievano, E. Fonda, F. Jaouen, *Nature Materials* 14 (2015) 937-942.
- [45] T. Ikeda, M. Boero, S.-F. Huang, K. Terakura, M. Oshima, J.-i. Ozaki, *The Journal of Physical Chemistry C* 112 (2008) 14706-14709.
- [46] Y. Okamoto, *Applied Surface Science* 256 (2009) 335-341.
- [47] M.F. Francis, W.A. Curtin, *Nature Communications* 6 (2015).
- [48] Q. Jia, N. Ramaswamy, H. Hafiz, U. Tylus, K. Strickland, G. Wu, B. Barbiellini, A. Bansil, E.F. Holby, P. Zelenay, S. Mukerjee, *ACS Nano* 9 (2015) 12496-12505.
- [49] K. Artyushkova, B. Kiefer, B. Halevi, A. Knop-Gericke, R. Schlögl, P. Atanassov, *Chemical Communications* 49 (2013) 2539-2541.