The Direct Ammonia Fuel Cell and a Common Pattern of Electrocatalytic Processes

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A record power density of 450 mW/cm² has been demonstrated for a direct ammonia fuel cell using an alkaline membrane electrolyte. The relative activities of Pt-based and Ir-based AOR catalysts are determined by a lower onset potential at Ir, explained by the higher bond strength Ir-N vs. Pt-N. This beneficial effect of the higher bond strength overrides the opposite effect on the rate of surface dimerization. A mechanistic pattern common to the AOR, ORR, and HOR processes is shown to involve a pre-step preceding the RDS, where the former step is the determinant of the onset potential. This pattern and the role of the pre-step in determining both the onset potential and the form of polarization curves observed for electro-catalytic processes are revealed from rate expressions based on absolute rate theory, with a pre-factor reflecting the dependence of the surface populations of active sites and/or reactants for the RDS. A brief discussion of choices of “single descriptors” which have been proposed for such complex electrocatalytic processes suggests that an elaborated description of these processes would require, as a rule, more than a single descriptor. Recognition of Ratko Adzic’s career achievements means celebration of Electrochemistry, a discipline which has seen great advancements over the time span of Ratko’s career, to a significant degree thanks to his excellent personal contributions. Over the years, I have been involved in this field as a fuel cell scientist and technologist and my perspective of work done on electrocatalyst development and characterization has been determined, to a large degree, by its impact on polymer electrolyte fuel cell (PEFC) technology. A common introduction section in papers on electrocatalysis in PEFCs describes an ultimate cost target of $30/kW for the fuel cell stack in a passenger vehicle and the major contribution of the PGM catalyst to the high cost of the stack at present. This then serves as explanation for the critical need to further develop metal electrocatalysts of higher mass activity to achieve further reduction in the loading of PGM catalysts needed per kW generated, as required for reasons of high price and limited global availability of these metals. The reduction over the last 40 years by a factor of ~100 in the mass of platinum needed per kW generated in a PEFC can be traced to several key milestones. The first was the invention of carbon-supported Pt catalysts prepared by colloidal chemistry techniques, the second was the invention of composite catalyst layers made of a mixture of catalyst and ionomer, the third was the discovery of ORR rate enhancement by alloying Pt with transition metal atoms, and the latest has been maximization of Pt utilization by use of a Pt shell on a nanometer size non-PGM core. Ratko Adzic’s contribution to the latter technology has opened a wider door for reduction of the Pt loading in a PEFC stack for transport applications, down to 0.2 gPt/kW, with good prospects for further lowering to 0.1 gPt/kW in the next 2–3 years. This status of PEFC electrocatalyst technology has been confirmed in 100 kW stacks, powering Fuel Cell Electric Vehicles (FCEVs) that entered the passenger vehicle market ~3 years ago. The arrival of these first FCEVs, manufactured by Toyota, Hyundai, and Honda, has signaled success in overcoming key barriers to market entry, with the tallest being the cost barrier associated primarily with the Pt electrocatalyst. Indeed, once the total requirement of Pt for a 100 kW PEFC stack comes down to 10 g, the corresponding Pt price of ~$300 per passenger vehicle becomes quite acceptable, and concern about Pt availability subsides, recognizing that a similar mass of Pt is being used in catalytic converters of ICE powered vehicles which are to be replaced by the FCEV. This updated perspective does not mean that no further efforts are required to complete the development of a PEFC technology based on ultra-low PGM loadings. Challenges of long term catalyst stability and of localized mass-transport limitations have been recognized in operation of air cathodes with Pt loadings of 0.1 mg/cm² or below. Air cathodes based on such low loadings, with the PGM catalysts prepared in various different ways, have been under investigation for stability and oxygen transport limitations. In these two regards, the Pt shell / non-Pt core catalysts prepared by Adzic et al., have an advantage of maintaining a higher overall surface area of the catalyst when the overall Pt mass is drastically lowered, thereby reducing localized mass-transport limitations. The stability challenge, considered the most demanding for core-on-shell structures, has been recently effectively addressed by Adzic et al. With PEFC stack technology having now advanced to the point of confidence in the high performance and low cost targets, heightened attention has been paid to the hydrogen infrastructure demands of FCEVs. For electrocatalysis R&D work, the consequence has been the recently expanded efforts devoted to catalysts for water electrolyzers and the development of new types of electrocatalysts that would be required when other fuels are considered for use in FCEVs. Pursuit of such other fuels has been the result of the challenges of highly compressed hydrogen gas used as a fuel for transport. Some new initiatives have targeted fuels which are in liquid form under ambient or near-ambient conditions, which would facilitate significantly fuel distribution and refueling. Ruling out fossil fuels and CO₂ emissions, and aiming for a high air quality, such fuels would be fabricated using renewable energy sources and would have zero tail pipe emissions. An ARPA-E (US DOE) program named REFUEL, targeting such liquid fuels as possible alternatives to compressed hydrogen, started in 2017. Part of this program is a project devoted to the development of a direct ammonia fuel cell (DAFC) which uses ammonia as a direct feed to the cell anode. This project provided me with an opportunity to collaborate with Ratko Adzic, who has shared with Jia Wang the responsibility for the development at BNL of an ammonia oxidation reaction (AOR) catalyst for use in the DAFC anode. An AOR catalyst which would generate high specific activity at low temperatures is quite a tall order, and significant performance advancements made over the first year of the project, side-by-side with the development of a deeper understanding of the AOR process, are described in this paper. These understandings are further used as the basis for this discussion of general aspects of electrocatalysis. This paper also addresses the practical target of bringing the performance of the anode in a DAFC to © The Author(s) 2018. Published by ECS. 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the level required for use in a fuel cell for transport application. And, in addition, having chosen an alkaline membrane electrolyte for the DAFC developed in this project, another aspect of electrocatalysis in our recent work has been the use of non-PGM catalysts for the DAFC cathode, as enabled by the alkaline environment of the cell. ORR fundamentals in base solutions have been studied to a much lesser degree than the same process in acid solutions and some insights in this regard are offered here. The rate equations presented here for the ammonia oxidation and oxygen reduction reactions reflect the complete dependence of the current on electrode potential, highlighting a common pattern in the mechanism of electrocatalytic processes.

The Ammonia/Air Fuel Cell and the Ammonia Oxidation Reaction (AOR)

The AOR mechanism, rate equation, and practical considerations.—Ammonia has been considered before as a potential fuel for transport applications, although actual use of ammonia as a fuel for transport took place only in cases of extreme shortage of common fuels, for example in Belgium during WWII. A recent re-examination of ammonia as a potential fuel for transport took place only in cases of extreme shortages of common fuels, for example in Belgium during WWII. A further electro-oxidation of ammonia is not included in the anode process described, as such oxides are reported to form under anode potentials well beyond 0.5 V vs. RHE, i.e., well beyond the maximum potential expected of a well functioning DAFC anode at $T_{\text{cell}} > 60^\circ\text{C}$.

As to the present understanding of the rather complex AOR process taking place at the DAFC anode, there is significant evidence supporting the identity of possible steps in the electro-oxidation of ammonia that are described in Scheme 1. This scheme also depicts the energy changes associated with each AOR step included in this scheme as evaluated by Mavrikakis et al. from DFT-based calculations for (111) surfaces of Ir and Pt catalysts. Siddharth et al. described in a recent paper the spectroscopic identification of various surface intermediates in the direct ammonia fuel cell (DAFC) anode. Indeed, examination of the AOR in a “half-cell”, i.e., probing the characteristic of the catalyzed electrode immersed in an aqueous alkaline solution containing ammonia, reveals an “onset potential” for the AOR at Pt catalysts near room temperature, exceeding 0.4 V vs. RHE. In a first order evaluation of the prospects of the DAFC based on such recent reports, the substantial inferiority of the performance of such anodes compared to the performance of a hydrogen anode in a H2/ Air cell would be cause for significant concern.

The discussion offered here of the rate of the AOR and its dependence on the nature of the anode catalyst and other anode parameters has two goals. One is to examine the understandings and conclusions regarding AOR catalysis reached by using combined experimental and theoretical tools. The second goal is “reduction to practice” of DAFCs which would depend, to large degree, on what can be practically done to shrink this gap of 0.4 V in onset potential between an ammonia and a hydrogen anode.

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*NH*₃ (or *NH*) and yielding nitrogen and water as final products, was proposed by Maurer and Gerischer and is known as the Maurer-Gerischer (M-G) mechanism. Active site blocking, brought about by exposure of the AOR anode to potentials higher than ~0.5 V vs. RHE, has been confirmed by the observed anode deactivation following exposure of the anode to such higher potentials. This deactivation can apparently be reversed reductively, for example by temporary opening of the circuit. However, continuous operation of the ammonia anode with minimal formation of surface poison is clearly preferable and achieving this target requires anode operation within a narrow potential range between the AOR onset potential and the onset of significant poisoning effects. This last limitation makes the target of an active and stable ammonia anode particularly challenging, as the low rate of the AOR cannot be readily enhanced by application of higher overpotentials because of the risk of catalyst poisoning.

Given this qualitative description, it would be instructive to look at an equation describing the rate of the AOR, derived based on the sequence projected by M-G, and depicted in Scheme 1 together with the calculated step energies for the (111) crystal surfaces. Indeed, the Pt(100) crystal surface is known to exhibit AOR activity significantly higher than that of Pt(111), but the calculated energy changes shown in Scheme 1 for the steps of the AOR at the (111) crystal surface represent much better the energetics expected at the polycrystalline surface of a dispersed Pt (or Ir) anode catalyst. These calculated step energies clearly suggest that at least at the (111) surface the lowest energy route for conversion of NH₃ to N₂ + H₂O involves formation with subsequent dimerization of an NH₂ surface species. With the dimerization step calculated to have the highest activation energy along this route, (see Scheme 1), the rate of NH₂ dimerization, and consequently the rate of the overall process of anodic oxidation of NH₃ to N₂ + H₂O, is expected to be given by:

\[
d[N₂H₄]/dt = k_1[NH₂] \exp(-\Delta G_{\text{dimm}} / RT)
\]  

This expression assumes a coverage independent activation energy for the dimerization step and it is also assumed here that surface poisoning is kept negligible by operating the anode within a potential window securing stable AOR faradaic current.

The surface coverage by the NH₂ species can be derived, in turn, considering that it is formed by a reversible step preceding the RDS, as suggested by the calculated changes in free energy depicted in Scheme 1. This type of “pre-step” is common in the mechanisms of electrocatalytic processes, as further discussed in this paper. A steady state surface coverage by NH₂ can be expressed as function of the reactant concentrations and the anode potential, by

\[
θ_{\text{NH}_2} = K_1(1 - θ_{\text{NH}_2}) [NH_3] [OH-] \exp(\exp(\frac{\Delta G_\theta}{RT}))
\]

where \(K_1\) is the value of the ratio \(\theta_{\text{NH}_2}/(1-\theta_{\text{NH}_2})\) for a catalyst in contact with an electrolyte of 1 M ammonia and 1 M hydroxide, under anode potential \(E_{\text{an}} = E^{\ast}_{\text{NH}_2} / \text{NH}_3\).

The rate of the NH₂ dimerization step can hence be written as:

\[
d[N_2H_4]/dt = k_1 [K_1(1 - θ_{\text{NH}_2}) [NH_3] [OH-]]^2 \times \exp\left[\left(\frac{2F}{RT}\right)(E_{\text{an}} - E^{\ast}_{\text{NH}_2} / \text{NH}_3)\right] \times \exp\left(-\frac{\Delta G_{\text{dimm}}}{RT}\right)
\]

The reaction order expected vs. ammonia when measured at a constant anode potential vs. a reference potential independent on NH₃, activity, a condition met by the RHE, is calculated from Eq. 3 as:

\[
(d \log J / d \log [NH_3])_{E_{\text{an}} \text{vs. RHE}} = 2
\]

The reaction order expected at constant \(E_{\text{an}}\) vs RHE defines the reaction order vs. the same anode reactant for the overall fuel cell process, measured for this case as \(d \log J / d \log [\text{NH}_3]\) \text{Vol.} and, consequently, it is the relevant measurement for gauging the expected effect of the anode reactant concentrations on the performance of the NH₃/O₂ fuel cell. According to Eq. 4, at given \(E_{\text{an}}\) vs RHE, the rate of the AOR can be increased substantially by increasing the concentration of ammonia, with such increase having full effect near the AOR onset potential, where the fraction of free catalyst sites at steady state, \((1-θ_{\text{NH}_2})\), is near 1. Consequently, an important expected benefit of such concentration increase is an earlier AOR onset potential.

For OH-, the reaction order expected from Eq. 3, measured at constant anode potential vs. a reference potential independent on OH- activity, e.g., at constant potential vs. SHE, is (assuming \(k_1\) is not a function of [OH-]),

\[
(d \log J / d \log [OH^-])_{E_{\text{an}} \text{vs. SHE}} = 2
\]

and, when measuring the effect of [OH-] on the AOR current at constant \(E_{\text{an}}\) vs RHE, the negative shift of the RHE potential with increase in [OH-] will result in zero order behavior

\[
(d \log J / d \log [OH^-])_{E_{\text{an}} \text{vs. RHE}} = 2 + \left(\frac{2F}{RT}\right)\left(\frac{dE_{\text{RHE}}}{d \log [OH^-]}\right) = 0
\]

In a multistep process involving a sequence of coupled OH- ion and electron transfer steps, the current is expected to be independent on the concentration of OH- at constant \(E_{\text{an}}\) vs. RHE, as borne out by Eq. 6. However, this is not the behavior observed experimentally for the AOR, as was reported by Katsounaros et al. The latter paper proposed an explanation for this unusual behavior based on a mechanism involving the formation of active adsorbed intermediates by coupled transfer of two hydroxide anions and one electron. Such reaction would generate negatively charged "NH" type intermediates instead of the neutral surface species formed by coupled transfer at ratio OH-/e = 1. However, once the final neutral products of the AOR process form via any type of adsorbed intermediate, the overall number of OH- and e transferred to the ammonia reactant molecule to form these neutral final products must be identical. Since the AOR current measured is generated by the complete AOR process, it is not obvious why an expected ratio 2:1 of OH- : e transfer in the formation of the active intermediate would result in non-zero dependence of the overall AOR current on [OH-] under constant \(E_{\text{an}}\) vs RHE. As discussed below, in electrocatalytic processes the step of formation of the active intermediate determines the onset potential, whereas the overall kinetics and, therefore, the reaction orders for the overall faradaic process, are determined by the next step, the RDS.

A possible alternative explanation is the effect of the concentration of K⁺OH⁺ on the value of the rate constant for the AOR (\(k_1\) in Eq. 3). Such a beneficial effect of higher concentrations of KOH on this rate constant could have to do with the repulsion of OHaq reagent anions by the negative surface charge documented for a Pt catalyst in alkaline medium at low potentials. At higher K⁺OH⁺ concentrations, the potential profile at the catalyst-electrolyte interface could be altered favorably for easier access of OHaq to the catalyst surface. Such an effect can be written as a modification of Eq. 6, for conditions where the rate constant, \(k_1\), is significantly affected by base concentration

\[
(d \log J / d \log [OH^-])_{E_{\text{an}} \text{vs. RHE}} = (d \log J / d \log [KOH])_{E_{\text{an}} \text{vs. RH}}
\]

Another possible reason for an increase of the rate constant with an increase in the base concentration is an increase of the activity coefficient of OHaq at high base concentrations.

Considering the net benefit to DAFCA performance of increased reactant concentrations, Eq. 4 suggests that an ever higher concentration of ammonia should help to strongly increase the AOR rate at constant anode potential vs. RHE and, therefore, the performance of the NH₃/O₂ fuel cell. The second order dependence of the anode current on [NH₃] suggests, for example, that a x 100 increase in DAFCA current could be achieved at a constant fuel cell voltage with 10x increase in the ammonia feed concentration. Because raising the OH- ion concentration results in an increase of the rate of the AOR at constant \(E_{\text{an}}\) vs RHE (Eq. 7), it also increases the DAFCA current at constant cell voltage. Raising the base concentration is projected to have a milder effect and, furthermore, the higher concentrations of OH- may negatively affect the relative rates of the desirable NH₂ dimerization process and the undesirable electro-oxidation processes which consume "NH₂ to form surface poisons (as noted above, the latter processes have not been considered in the derivation of Eq. 3).
Consequently, maximizing the concentration/partial pressure of ammonia and using optimized concentrations of the base, seems to be the general formula for a substantial increase in AOR performance vs. that observed with low concentrations of ammonia and base, typically used in lab cell investigations.

Another requisite for reaching the DAFC performance demanded of power sources for transport applications is operation of the cell near the high temperature limit determined by (i) the limited chemical-thermal stability of ionomers and of graphite or metal hardware materials used in a membrane electrolyte fuel cell and, (ii) the strong preference for cell operation at internal pressures close to ambient. Based on these criteria, the highest operation temperature of a polymer electrolyte DAFC is near 100°C. When the beneficial effects of higher cell temperature and high reactant concentration are combined in a DAFC benefiting from good quality MEAs and effective water management, the resulting BOL performance obtained recently is presented in Fig. 2. The performance seen at low currents is limited because of the excessive rate of cross-over of the anode liquid medium into the cathode, requiring further optimization of the membrane and operation conditions. However, the peak power generated of 450 mW/cm² provides significant confidence in the prospects of a direct ammonia fuel cell operating near 100°C serving as power source in transport application.

A common pattern in the mechanism of electrocatalytic processes.—A characteristic pattern in the mechanism of electrocatalytic processes which is clearly recognized in the mechanism of the AOR is a surface redox step preceding the RDS. It can be readily seen from Fig. 2 that the RDS activation energy is not potential dependent. However, as shown below, pre-steps of a similar nature determine the onset potential for other electrocatalytic processes where the RDS involves charge transfer (for example in the ORR).

This characteristic behavior of a surface redox pre-step followed by the RDS has important bearing on the relative activities of various catalysts in a given electrocatalytic process. This has not been recognized in calculations of electrocatalytic activity that are typically based on the highest activation energy of a step in a specific multistep sequence identified as requiring the least energy. The activation energy is used as the yardstick for the “Activity” of a given catalyst, with the “Activity” calculated in terms of a rate constant, $k$, as

$$k = \nu \cdot (E_{\text{onset}}/2.3RT)$$

with $\nu$ representing a general frequency factor. In a comprehensive expression for the rate of the electrocatalytic process such general frequency factor is replaced by a potential dependent term which, in the specific case of the AOR, is given by Eq. 3, as

$$k = K \cdot (1 - \theta_{\text{NH}_2}) \cdot (E_{\text{an}} - E^*_{\text{NH}_2/NH}) \cdot \exp(2F/RT)$$

Consequently, unlike the “Activity” values calculated from Eq. 8, the actual AOR current at a given $E_{\text{an}}$ may be determined to a large degree by the value of the onset potential, which is determined, in turn, by the value of $E^*_{\text{NH}_2/NH}$. Conclusions on the relative activities of metal catalysts based solely on the activation energy of the RDS, may therefore miss an overriding effect of the onset potential.

An example of such an effect is provided by the relative activities of Pt and Ir in the AOR process. Pt has been projected from DFT calculations to have the highest AOR activity, specifically, higher than the activity of Ir, as reflected by the volcano plot included in Ref. 8 and shown in Fig. 3. This was concluded from the activation energy of the “NH2 dimerization process (the RDS), calculated to be lower at Pt than at an Ir catalyst surface. Experimental measurement of AOR activity do not agree with this order of activities: Iridium based anode catalysts exhibit higher activity in the AOR, as demonstrated in Fig. 4, with the Ir advantage increasing with an increase in cell temperature. The reason for this apparent discrepancy becomes clear when considering the full expression for the AOR rate, as given in Eq. 3. While the higher Ir-N bond strength results in a higher AOR activation energy, $\Delta G^\#_{\text{dim}}$, it enables at the same time onset of the AOR process at a lower anode potential, because the pre-RDS step of “NH2 intermediate formation is facilitated by the higher Ir-N bond energy (see Scheme 1). The net result of these two opposite effects of the metal-nitrogen bond strength can be estimated from the relative magnitudes of the differences ($\Delta G^\#_{\text{dim}}$)Ir - ($\Delta G^\#_{\text{dim}}$)Pt and, F[(E^*_{\text{NH}_2/NH})Ir - (E^*_{\text{NH}_2/NH})Pt]. From the calculated step energies in

Figure 2. Performance of a Direct Ammonia (NH3/O2) Fuel Cell at $T_{\text{cell}}$ = 100°C. The PGM anode loading was 2 mg per cm² and the cathode was catalyzed by a non-PGM catalyst (Cell construction and testing by Ben Achrai and Gal Tamir of POCellTech).

Figure 3. A volcano plot based on calculated activation energies for the RDS in the ammonia anodic oxidation process that, according to the Maurer Gerischer mechanism, is the dimerization of “NH2 to form “N2H4.8
AOR in NH3-saturated 1 M KOH, 60 °C

Figure 4. Mass activity of metal catalysts in the AOR as a function of anode potential for carbon supported Ir, IrPt, and two Pt catalysts. Ir catalysts exhibit significantly higher activity than Pt thanks to the lower onset potential of the AOR, as explained by the lower expected $E^\circ_{NH2NH2}$ for Ir (Jia Wang et al. at BNL, The ARPA-E, DAFC Project, 2018).

Scheme 1. ($\Delta G_{\text{b}}^{\text{diff}, \text{hr}}$ - $\Delta G_{\text{b}}^{\text{diff}, \text{hr}}$)Pt = +0.14 eV and, $F(\left(E^\circ_{\text{NH2NH2}}\right)^{\text{hr}} - \left(E^\circ_{\text{NH2NH2}}\right)^{\text{hr}})_{\text{Ir}} = -0.29$ eV, explaining the activity advantage of iridium in the AOR.

Interestingly, the community involved with advanced calculations of bond and activation energies in electrocatalytic systems has used different tools for identification of the process defining the onset potential for a multistep electrocatalytic process. The latter approach resorts to a distinction between “kinetic factors” and “thermodynamic factors”, where the latter factors determine the onset potential.17-19 The “thermodynamic factor” boils down to the free energy change associated with a step of formation of an adsorbed intermediate of surface population varying with potential in a form characteristic of a surface redox system. Such intermediate formation steps are similar in nature to the pre-steps described here. However, the rate diagnostics presented here show that analysis based on absolute rate theory alone, as applied to multi-step processes involving charge-transfer, yields directly the full expression for the rate of the overall process, as determined together by the onset potential and the activation energy of the RDS. The only pre-requisite for obtaining the full rate expression described here is proper consideration of the potential dependence of the pre-factor in the rate expression.

As a final comment regarding the experimental study of the AOR, it can be seen from Fig. 4 that a PtIr catalyst exhibited higher AOR activity at 60 °C than either Pt or Ir. This observation suggests further study of the AOR activity at PtIr, as well as other PtIr catalysts, as needed to improve the fundamental understanding of this electrocatalytic process and thereby increase the mass activity of such PGM anode catalysts. One possible reason for the beneficial effect of combining Ir and Pt in the AOR catalyst is that the higher Ir-N bond strength goes hand in hand with a higher Ir-O(H) bond strength, possibly resulting in competition for Ir surface sites by adsorbed OH. Consequently, the AOR activity at higher anode potentials could be higher on the Pt sites in a PtIr catalyst and such a catalyst could thus combine a lower onset potential, facilitated by Ir surface sites, with a stronger rise of the catalyst activity with anode potential which may be facilitated by Pt surface sites.

The Fuel Cell Cathode Process

Onset potential and RDS in the ORR.—The ORR is undoubtedly the most studied fuel cell process, both experimentally and theoretically. Insights offered here center on the role in the ORR mechanism of a pre-step preceding the RDS as determinant of the onset potential and of the form of the voltage-current dependence. The similar role such pre-steps play in two electrode processes as different as ORR and AOR suggests that they are common in mechanisms of multi-step electrocatalytic processes. This should not be too surprising considering that the electrocatalyst surface in contact with the relevant electrolyte and reactants has, under open-circuit conditions, a composition which does not allow immediate onset of the faradaic process and, consequently, requires pre-conditioning, driven by the overpotential, to “prepare the stage” for the RDS. To examine the nature of the pre-step which determines the onset potential for the ORR at Pt, a sequence of ORR steps in acid is described in Scheme 2, that considers all processes of Pt-OH (and Pt-O) formation and reduction taking place at a Pt surface in contact with H2O and O2 in the relevant potential range.

The bold face •OH, shown to be reduced in Step 1, designates the surface species formed on Pt at open circuit by a reaction involving both water and dioxygen

$$\text{•OH} + \frac{1}{2} \text{O}_2 = 2\text{(•OH)}$$

with possible conversion to a surface oxide species, by: 2 (•OH) = H2O + •O2.

At Pt in contact with oxygen-free water, the same surface species is formed quasi-reversibly by “water discharge”

$$\text{•OH} + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O} + \text{e} + \text{H}^+$$

as reflected by the pseudo-capacitive currents of the Pt voltammogram.

At potentials above 0.75 V, the surface population of the •OH species at Pt becomes substantial, blocking free metal sites needed for Step 2 in Scheme 2, which has been identified experimentally as the RDS for the ORR. The process in Step 1 which precedes the RDS generates active metal sites – a prerequisite for the onset of the process of the RDS (Step 2) – and the role of Step 1 can therefore be described as the “ignition” of the ORR process. Consequently, once Scheme 2 is recognized as the actual mechanism for the ORR at Pt, the standard potential of the surface redox couple activated in Step 1 (see Eq. 10) defines the onset potential for the ORR.

An expression for the complete dependence of ORR current at Pt on the cathode potential that considers a potential-dependent active site population was described earlier.18-19 The expression can be written in general form for a cathodic process as

$$J(E) = Cr \exp(F \varepsilon^{\text{act}}_{\text{cat}}) \times (E - E^{\circ}_{\text{surf}, \text{redox}}) \times \exp(-[\Delta H^{\text{act}}/2.3RT]) - \frac{(E_{\text{cath}} - E^{\circ}_{\text{surf}, \text{redox}}/b)}{[11]}$$

where $E^{\circ}_{\text{surf}, \text{redox}}$ is the standard potential for the surface redox system established in the process preceding the RDS. The dependence of the redox system population ratio, $Z = [\text{OX}]/[\text{RED}]$, on $E_{\text{cath}} - E^{\circ}_{\text{surf}, \text{redox}}$, can be written for a 1e surface redox system obeying the Nernst equation, as

$$Z = \exp(F/RT) \times (E_{\text{cath}} - E^{\circ}_{\text{surf}, \text{redox}})$$

and, with the population of the reduced form of the redox couple i.e., the active form in a cathodic process, given by (Z+1)$^{-1}$, Eq. 13 below describes the full dependence of the ORR current on the cathode potential, $J = C_r \exp(F/RT) \times (E_{\text{cath}} - E^{\circ}_{\text{surf}, \text{redox}}) \times [(E/RT) - (E_{\text{cath}} - E^{\circ}_{\text{surf}, \text{redox}})]$.

A mechanism for the ORR at a Pt catalyst (a free Pt site is designated by *).
For a metal/metal hydroxide redox system, M/MOH, the pre-factor, \(\{\exp (F/RT) (E_{\text{cath}} - E^0_{\text{surf redox}}) + 1\}\)^{-1}, describes the functional dependence of \(\theta_M\), the fractional surface population of free metal active sites, on \(E_{\text{cath}}\), exhibiting a sigmoidal form with \(\theta_M = 0\) at high \(E_{\text{cath}}\), \(\theta_M = 1\) at low \(E_{\text{cath}}\) and the inflection point of the sigmoid located at \(E^0_{\text{surf redox}}\). Recognizing the active site as a reactant in the RDS (Step 2), it can also be stated that the pre-factor in Eq. 13 reflects the potential-dependent population of a reactant in the RDS, as is the case in the AOR.

The potential dependent slope of the \(\log j\) vs. \(E_{\text{cath}}\) plot expected from Eq. 13, is
\[
\frac{d\log J_{\text{ORR}}/d(-E_{\text{cath}})}{d(-E_{\text{cath}})} = b_{\text{apparent}} = 1/b + d\log \theta_M/dE_{\text{cath}}
\]
which can be written, in turn, as
\[
1/b_{\text{apparent}} = 1/b + d\log \theta_M/dE_{\text{cath}}
\]
where \(b\) is the “intrinsic” Tafel slope, expected for a Pt catalyst with a potential-independent population of active sites. It can be seen that the apparent Tafel slope, \(b_{\text{apparent}}\), has a value determined by two different effects of the overpotential, the lowering of the activation energy of the RDS and, the generation of active metal sites by potential driven reduction of Pt-OH.

The plot of \(\log J_{\text{cath}}\) vs. \(\eta_{\text{cath}}\) shown in Fig. 5 was derived using the dependence of free Pt site population on potential, derived, in turn, from the Pt cyclic voltammogram and assuming a potential independent slope of \(d\log J_{\text{cath}}/d\eta_{\text{cath}} = 120\) mV/decade at a catalyst surface with non-variable population of active sites. The plot has the recognized pattern of low apparent Tafel slope at lower currents, gradually increasing with overpotential to reach, at high current densities, the value of 120 mV/decade, which is expected when the surface population of active Pt sites has reached its maximum possible value, \(\theta^*_\text{cath}\).

This pattern is observed for ORR processes at other metal catalysts, as well as at completely different types of catalysts, for example carbon-supported metal ion centers, as shown in Fig. 6. This similarity suggests that these electrocatalytic processes can be all described as “surface redox mediated” and this mechanism is applicable to metal catalysts much the same way as to carbon supported ionic centers. In such a redox-mediated process, as the overpotential is increased the current is expected to rise significantly above zero only when \(E_{\text{cath}}\) approaches \(E^0_{\text{surf redox}}\) and the continued increase in population of active sites with over-potential is expected to result in low values of \(d\log J_{\text{cath}}/d\eta_{\text{cath}}\) at lower current densities (Eq. 14).

The significance of Step (1) in Scheme 2 in defining the onset potential for the ORR at Pt and in defining the form of the voltage-current relationship observed for this process, should be quite clear from the discussion above. Nevertheless, this step has been ignored in mechanisms proposed for the ORR, that largely ignored the site blocking effect of the *OH and *O species formed at a Pt surface by water discharge. This includes mechanisms used in more recent analyses based on DFT calculations. One consequence of disregarding Step (1) in the ORR mechanism is the challenge encountered in the interpretation of volcano plots describing the ORR activity as function of the M-O bond strength (see Fig. 8) The ascending branch of the volcano plot for the ORR describes, for a series of metal surfaces of significant affinity to oxygen, an increase in calculated catalyst activity with weakening of the M-O bond. This implies that the step in the ORR which determines the “Activity” for metals on the ascending branch, including Pt, involves breaking of a M-O or M-OH bond. As the RDS of the ORR at Pt has been identified experimentally as Step (2) in Scheme 2, which involves M-O bond formation rather than bond scission, the RDS step cannot be the determinant of ORR activity which, according to the volcano plot in Figure 8, is facilitated by scission of a M-O bond. Recognizing Step 1, which involves scission of a M-Ox bond, as determinant of the onset potential for the ORR, provides a direct explanation for the position of Pt near the top of the ORR volcano plot, only requiring the “activity” to be determined by the M/MOH redox potential, rather than by the activation energy of the RDS. The latter condition is well fulfilled for metals, including Pt, on the ascending branch of the volcano, for which a higher M/MOH potential corresponds to a higher ORR activity. In contrast, as long as Step 1 is not considered as first step in the ORR mechanism, the explanation for the position of Pt near the top of the volcano plot becomes significantly less straightforward.

Finally, when examining the actual (rather than calculated) relative activity of ORR electrocatalysts, removal of blocking surface oxygen species is clearly revealed as the determinant of the activity. The experimentally determined onset potential for the faradic ORR current is well correlated with the onset of the electroreduction of blocking hydroxide and oxide species, as seen in voltammograms recorded for the same electro-catalysts in an oxygen free electrolyte. For this purpose, the Pt voltammogram needs to be recorded with the high end potential limited to 1.0 V to show the onset of reduction for the surface hydroxide/oxide layer formed at the potential experienced by the Pt catalyst in a fuel cell cathode. An example is provided in Fig. 7. The figure shows, for the case of Pt(111) and PtNi(111), an onset potential for the faradaic ORR current which is well correlated with the onset potential of surface hydroxide reduction. The key benefit of the lowered surface affinity to oxygen achieved by alloying Pt with Ni is, therefore, the lower cathode overpotential required for the formation of active free Pt metal sites. Examining Eqs. 13, this means that the shift of \(E^0_{\text{surf redox}}\) in this case \(E^0_{\text{M/M-OH}}\) to higher potentials
bond strength as single descriptor for the electrocatalytic activity of a process. For example, the well documented identification of the M-X bond strength as single descriptor may not explain the activity ranking observed experimentally. An example is the case described above for the AOR process at Pt and at Ir catalysts. The single descriptor for the process, used as the variable for the relevant volcano plots, is the M-N bond strength. However, while Pt has been projected to be the more active catalyst thanks to the weaker M-N bond strength facilitating the surface dimerization process in the RDS, Ir has been determined experimentally as more active in the AOR, explained by a lower onset potential enabled by the stronger Ir-N bond. This example clarifies that, having identified a specific surface bond as “descriptor” for an electrocatalytic process, leaves additional factors to be considered before reaching conclusions on relative activities. Another example is the conclusion offered, based on identification of “thermodynamic factors” affecting the rate of the ORR,\textsuperscript{18,19} that a step of Pt-OH reduction to Pt+H2O defines the onset potential for the faradaic process. This leaves an open question regarding the identity of this Pt-O bond-breaking step in the ORR sequence. This identity remains unclear as long as Step (1) in Scheme 2 is missing in the ORR sequence considered (see, for example, Refs.\textsuperscript{18} and 19).

Another interesting challenge to the use of the M-O bond strength as single descriptor for the ORR is presented by the high ORR activities observed experimentally for various metal catalysts with the M-X bond strength. However, correlating the relative activities observed experimentally for various metal catalysts with the M-X bond strength as single descriptor may not explain the activity ranking observed experimentally. An example is the case described above for the AOR process at Pt and at Ir catalysts.

Quite clearly, the common pattern identified here for electrocatalytic processes is insufficient, by itself, to fully characterize an electrocatalytic process. Recognizing this pattern facilitates identification of the step determining the onset potential and enables derivation of the current voltage relation. However, while the AOR, ORR, and HOR exhibit a common pattern of RDS preceded by a pre-step which determines the onset potential, these three processes are quite different in other important ways. For example, the RDS in the AOR is a unique, second order chemical process, the pre-step in the ORR is unique in generating active sites for the RDS, and the HOR has two possible pre-steps, with one operating at lower and the other at higher current density.\textsuperscript{23} This observation of a common feature which cannot characterize by itself a family of electrocatalytic processes is offered here as background for examination of the suggestion made repeatedly that a “single descriptor” can serve for effective characterization of an electrocatalytic process. This concept has received wide endorsement and is therefore interesting to probe if single descriptors proposed are indeed sufficient for the characterization of a specific electrocatalytic process. For example, the well documented identification of the M-X bond strength as single descriptor for the electrocatalytic activity of a diatomic X2 molecule at a M metal catalyst is certainly not counter-intuitive and has served for a long time as the variable determining the Activity in relevant volcano plots. However, correlating the relative activities observed experimentally for various metal catalysts in alkaline media (points above the descending branch of the plot).
The reaction step determining the onset potential.

effective description of the ORR activity requires further "descriptors’’, beyond the M-O bond strength. Yet another example of the need for further descriptors is provided by various electrocatalytic processes at non-PGM metal catalysts, which clearly require consideration of the strength of two surface bonds for an effective description of the electrocatalytic activity. For example, the HOR process at Ni-based catalysts requires both M-H and M-O bond strengths to be considered in order to properly account for the potential-dependent, competitive electro-sorption of H and OH/O species at Ni and Ni alloys in the relevant anode potential range. It would seem that the “single descriptor” concept was not seriously meant to apply to non-PGM metal, or metal alloy catalysts.

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