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New challenges in oxygen reduction catalysis: a consortium retrospective to inform future research

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In this perspective, we highlight results of a research consortium devoted to advancing understanding of oxygen reduction reaction (ORR) catalysis as a means to inform fuel cell science. We demonstrate how targeted collaborations between different institutions from academic, national lab, and industry backgrounds and different scientific disciplines like theory, experiment, and characterization can yield unique insights into fuel cell catalysts. We comment on such insights into material designs for platinum-group-metal alloys, transition metal oxides, and non-traditional materials including metal–organic frameworks; systems that have served as the foundational building blocks for our consortium. We also motivate a renewed focus on catalyst durability in light of emerging technological requirements and paths forward in understanding *in situ* and *operando* electrochemical stability. Finally, we describe new frontiers ORR research can take and how emerging artificial intelligence tools can assist researchers in capturing data, selecting new experiments, and guiding characterization to accelerate the design and discovery of fuel cell catalysts. A main goal of sharing this perspective is to discuss the rationale for our future research plans based on our consortium work. However, we also hope to illustrate both the potential impact of a collaborative strategy with the hopes of inspiring a higher degree of Industry-Academia-National Laboratory collaboration and encourage other centers and consortiums to distill and share their findings in a similar perspective-type article. Together we hope to enable the fuel cell research community to engage in a discussion of strategies for research and accelerated development of catalysts with improved activity and stability.

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Broader context

In fuel cells, the oxygen reduction reaction (ORR) is a bottleneck in devices that can help society transition to zero-emissions transportation. Current fuel cell technology has been sufficient to introduce fuel cell vehicles (FCEV) to consumers but still has significant room to improve, particularly with respect to ORR catalyst efficiency and durability. In recent years, fuel cell trucks have also become a more compelling technology for emissions reduction, but heavy duty vehicles have technical requirements for longevity and efficiency that surpass those of light duty vehicles. In this perspective, we summarize major scientific insights resulting from a consortium of researchers focused on the ORR. We also outline a future research strategy focused on understanding how and why catalysts degrade, motivated by both the requirements for longer-lasting fuel cell catalysts in trucks and by a compelling scientific frontier to understand the chemistry of catalyst stability using new experimental and theoretical approaches.

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1. Why the ORR continues to be important, yet challenging

1.1 Fuel cells and the limits of state-of-the-art ORR

Over 12 000 commercial fuel cell electric vehicles (FCEVs) fueled by hydrogen, rather than traditional fossil fuels or battery-stored electrical energy, are on roads in the US today.[1,2] Several factors limit the widespread adoption of FCEVs including high vehicle cost, lack of hydrogen fueling infrastructure, high cost of hydrogen production and distribution, and lower cost of battery EVs as a solution for zero emissions transportation.[3] While FCEVs have improved in both cost and performance, a number of technical challenges remain. Among the challenges, the performance of fuel cell catalysts remains a key limitation despite decades of research.

FCEVs rely on catalysts to improve both the hydrogen oxidation (HOR) and oxygen reduction (ORR) half reactions necessary to convert hydrogen into electrical energy. To be commercially viable, a catalyst must meet several criteria including sufficiently high activity, low cost, and long-term stability. Activity losses from HOR catalysts may result from impure H_2 feedstocks which poison active sites with CO, but state-of-the-art CO-tolerant PtRu materials have largely rendered HOR a solved problem for PEMFC.[4] For AEMFCs, the exchange current densities of Pt for HOR are orders of magnitude higher than that of ORR despite the fact that the HOR exchange current density is more than 2 orders of magnitude lower in strongly alkaline *vs.* strongly acidic electrolytes.[5] Thus, most recent fuel cell catalyst research has focused on improving and understanding the origin of activity for the ORR, which remains the bottleneck for fuel cell performance.

Activity is critical to fuel cells, and increasing catalyst activity results in increased power and efficiency, particularly because ohmic and mass transport losses are significantly lower than kinetic losses in fuel cells.[6] Electronic structure simulation has demonstrated that losses associated with conventional metal catalysts are imposed by the correlations between binding energies of surface adsorbates,[7] where even the theoretically optimal catalyst will show a substantial overpotential. New classes of catalysts that do not follow the adsorbate bond energy scaling relation of metals may substantially reduce the overpotential, but have yet to be realized experimentally.[8] Conventional platinum-group metal (PGM)-based catalysts are closest to the theoretical activity maximum and continue to be used in state-of-the-art fuel cell technology. Research centered on decreasing PGM loading to reduce costs has been largely effective, achieving US Department of Energy (DOE) loading targets of 0.025 $\text{mg}_{\text{Pt}}\ \text{cm}^{-2}$ and 0.1 $\text{mg}_{\text{Pt}}\ \text{cm}^{-2}$ for light-duty FCEV anodes and cathodes, respectively, and surpassing the corresponding mass activity target of 8 $\text{kW}\ \text{g}_{\text{Pt}}^{-1}$.[9] As such, state-of-the-art catalysts have low enough PGM loadings and high enough mass activities to introduce FCEVs to consumers.[10,11]

While the future of personal FCEVs would be brighter with enhanced catalytic performance and decreased PGM loadings, further engineering is needed to improve the durability of the fuel cell stack. The focus on durability is also motivated by technoeconomic analyses[12,13] that suggest FCEVs may be well-suited for heavy-duty vehicles. Designing fuel cells for heavy duty vehicles imposes different lifetime and manufacturing cost requirements than light-duty FCEVs. Heavy-duty trucks should have lifetimes in excess of a million miles traveled, or roughly 25 000 hours of operation. DOE targets for heavy duty FCEVs require a total Pt loading less than 0.3 mg cm^{-2} and end of life (EOL) performance of 2.5 $\text{kW}\ \text{g}_{\text{PGM}}^{-1}$. In the case of ICE-powered trucks, million-mile longevity is partially enabled by enhanced maintenance schedules and procedures relative to light-duty private vehicles. However, degradation of FCEVs is primarily in the fuel cell materials themselves, and as such it is not clear whether the lifetime of heavy-duty FCEVs can be improved by enhanced maintenance.

To summarize the state of the art of acidic ORR, we note that many of the most recent benchmarks in catalyst activity have resulted from nanostructuring.[10] More specifically, highly shape-specific octohedral nanoparticles,[14] multimetallic nanoframes,[15] and nanowires[16] have all increased the mass activity of conventional PGM-based materials. More recently, catalysts with unprecedented durability have been engineered using nitrogen-doping of conventional intermetallic PtNi.[17] Similarly, engineering the carbon support of ORR catalysts has also seen recent progress. State-of-the-art efforts in this vein have boosted fuel cell performance by improving transport in accessible carbon mesopores in order to reach the light duty DOE mass activity target.[9] Advanced durability has been reported from similar multi-functional catalyst supports (MFCS), including the above-mentioned DOE million-mile benchmarks for heavy duty vehicles.[18] In the case of non-metallic materials, state-of-the-art catalysts using MOFs as an active support have also been demonstrated with ultralow-loading of PtCo[19] and, more recently, engineered durability.[20]

In contrast, the primary advantage of alkaline fuel cells is that they are amenable to non-PGM catalysts, so benchmarks of catalysts for alkaline ORR differ from those of acidic ORR. Near and long-term DOE targets for alkaline fuel cells are summarized in ref. 21. The most performant alkaline FC membrane-electrode assemblies (MEA) still use Pt, and current state-of-the-art MEAs have 1.3 $\text{mg}_{\text{Pt}}\ \text{cm}^{-2}$ loading and peak power densities of 3,370 mW cm^{-2}.[22] State-of-the-art Non-PGM cathodes include transition metal oxide (TMO) materials like $CoFe_2O_4$[23] and $MnCo_2O_4$.[24] MEAs using these materials have reported peak power densities of 1350 and 1200 mW cm^{-2} respectively, still using 0.7 and 0.4 $\text{mg}_{\text{Pt}}\ \text{cm}^{-2}$ total PGM loading (*i.e.* for HOR). We note that reported fully PGM-free alkaline MEAs are currently less performant, typically between 10–100 mW cm^{-2}.[21] In addition, non-PGM materials like the aforementioned TMOs and recently reported Fe–N–C[25] have very limited reported stability testing in the literature for alkaline conditions.[5] However, PGM-free AMEFCs have already shown to be more performant and active compared to PGM-free PEMFCs, demonstrating the need for more research on the catalyst layers and the MEA assemblies for AEMFCs.

For further background on fuel cell catalysis, we refer the readers to recent reviews from the perspective of theory,[7] durability,[26] methodology,[27,28] and device-level research.[10,29] These reviews outline current understanding of ORR structure–property relationships, degradation and methodology for state-of-the-art catalysts, and the major technical milestones to achieving more practical FCEVs. As such, this perspective is not intended to exhaustively update the field on recent progress in fuel cell catalysis. Herein, we aim to demonstrate how broad and valuable insights can be derived from the close coupling of fundamental theoretical and experimental studies of ORR, to identify the extant needs of our fuel cell research community, and to outline strategies motivated by these needs for our, and other researchers', future efforts. Furthermore, we hope with this perspective that we can demonstrate the value in seeking out opportunities for large-scale collaboration and inspire current and future collaborative centers to distill and publish their most important insights from their years of working together.

1.2 New research must improve cost and stability

The main goals for continued ORR catalyst research, outlined in Fig. 1, can be condensed to (1) reducing material cost by decreasing PGM loading or finding non-PGM alternatives, and (2) increasing system lifetime by improving durability. While these are not new goals for the field, scientific understanding of one-off (or even multiple) catalyst activity and degradation analyses remains inadequate to efficiently predict and engineer novel materials that can outperform current benchmarks. Therefore, the next phase for ORR research must also focus on a new goal, (3) data-science driven efforts to accelerate catalyst design.

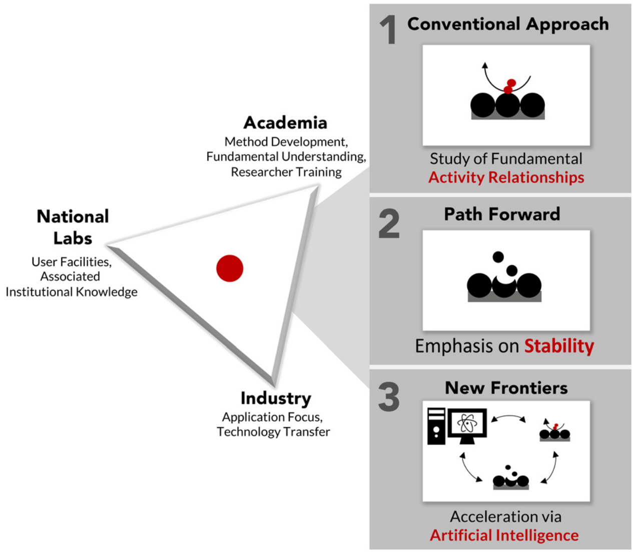


Fig. 1 Overview of TRI consortium that fosters collaboration between Industry, National Laboratories, and Academia and our research perspective on the role that the conventional approach to the design of ORR catalysts plays in development (Section 2), the paths forward for the ORR community (Section 3), and new frontiers that could accelerate the design of new catalyst materials (Section 4).

Addressing these three goals is challenging for a variety of reasons. Bringing data science tools to bear on PGM alternatives and catalyst durability requires the institutional capability to gather and curate large datasets related to libraries of materials, where both the costs and the risks of the research scale commensurately. While studies of activity can be performed in most university laboratories with small teams and modest resources, the characterization requirements to formulate convincing mechanistic hypotheses of catalyst degradation tend to require the use of user facilities such as synchrotrons housed at national laboratories due to their large infrastructural costs. Consortia as large as ours may not be strictly necessary, but generally we have observed that teams which combine specialized knowledge and capability from the fields of theory, synthesis, performance testing, microscopy, and spectroscopy are necessary to produce answers to the major fundamental questions for which our consortium was designed.

Standardizing durability benchmarks is also challenging, and will likely be necessary for data-driven prediction and analysis of ORR catalysis. Half-cell tests with liquid electrolytes and rotating disk electrodes (RDE), most useful for studying the basic science of ORR, do not strictly translate into durability tests in MEAs, and making inferences about relative performance between these two settings can be difficult due to differences in the catalyst's environment. For example, the 0.1 M KOH used to mitigate transport issues in RDE tests is lower than the 1 M KOH typically used to maximize the performance of alkaline fuel cells. Similarly, durability observed in MEAs, while a closer approximation to a FC-powered device, may not strictly translate into that observed after normal operation of an FCEV.[1] Analogously, it has been observed for certain catalysts that RDEs can significantly underestimate their performance relative to the realistic conditions observed in fuel cells, leading to undesirable false negatives.[30] Nevertheless, standardized accelerated stress testing (AST) is tremendously valuable to make meaningful comparisons between the results of different research groups on each level, and can be designed to approximate the effects of various elements of typical fuel cell operation, *e.g.* startup, shutdown, anode flooding, on various components of the catalyst layer, *e.g.* membrane, support, catalyst. We refer the reader to standard testing protocols for RDE,[31,32] MEA,[33] and device-level durability.[33]

Finally, the requisite domain knowledge to generate, curate, and use large structured digital datasets is a relatively new addition to most laboratory scientists' toolbox, providing an opportunity for specialists in industry and national labs to share their expertise in service of this pressing challenge. The challenge of advancing ORR catalysis research from exploratory basic science studies to more device-relevant applications motivated the formation of a consortium to coordinate and combine resources to address goals (1), (2), and (3).

1.3 Targeted collaboration is critical

In this manuscript, we describe the experimental and theoretical groundwork that a consortium of researchers from industry, national laboratories, and academia affiliated with Toyota Research Institute (TRI) has made towards the improvement of ORR catalysts. Alongside efforts to develop methodology to study performance and stability, we highlight new frontiers to use this foundational work to accelerate future catalyst development (Fig. 1). We see the primary strengths of this consortium as a focus on the hard problems that come with device-relevant materials research, approached with the tools and innovations of modern data science from the software industry. These software tools are utilized in tandem with the infrastructure of federal user facilities while maintaining the core concerns and mission of academia: an emphasis on fundamental insight and understanding of scientific phenomena. These diverse strengths, with coordination between relevant institutions, have been essential for distinctive advances in materials science,[34] including those detailed in this review.

The lessons learned from our targeted collaborations along with the research goals outlined in the previous section motivate the immediate path forward for our consortium, which is to focus on catalyst durability using the latest experimental and theoretical tools and to derive atomistic insights into why ORR electrocatalysts are stable or unstable. Furthermore, we lay out a vision for a next generation of artificial intelligence-assisted ORR catalysis research that intends to accelerate the rate not only at which we can discover new materials, but also understand and engineer the scientific phenomena that explain catalyst durability and activity.

Strategies to advance ORR catalysis science are not exclusive to our consortium. Indeed, it is our hope that our retrospective may inspire more academic researchers to adopt AI-based approaches that couple experiment and theory, for more user facilities to be considered as tools for collaboration, and for more companies to understand the progress that is possible when coupled to national labs and an academic network.

2. Conventional approach: fundamental activity relationships guide design of ORR catalysts

As described in the first section, development of state-of-the-art fuel cell catalysts like PtNi and PtCo has largely been successful, having both met research targets imposed by government agencies like the US Department of Energy[35] and having been sufficient to offer vehicles like the Toyota Mirai to consumers.[10] Furthermore, the development of these and other catalysts has benefited from the understanding of metal catalyst behavior from density functional theory (DFT), which predicts enhanced rates in both Pt–Ni and Pt–Co systems and rationalizes how the electronic structure of these materials place them near the optimum of ORR catalyst activity.[7] Therefore, the frontier for fuel cell catalyst development lies in reducing cost and increasing durability, both of which present scientific and engineering challenges.

To push beyond the state-of-the art of activity in oxygen reduction catalysis, our research consortium considered three avenues, summarized in Fig. 2, for improved materials for the ORR: (1) decreasing PGM content using *e.g.* core–shell nanostructuring, alloying, or tuning electrolytes, (2) optimizing traditional non-PGM materials using scaling relation analysis, high-throughput evaluation, and combined theory–experiment approaches, and (3) exploring non-traditional material spaces to understand new structure–property relationships and conduct more global searches for active ORR catalysts. Particularly in the case of categories (1) and (2), engineering efforts focus primarily on tuning the bond formation energies between catalyst and adsorbate, which in turn influences transition states and catalyst kinetics. Alternatively, these efforts may also target proton activity or dynamics in order to reduce proton transfer barriers.

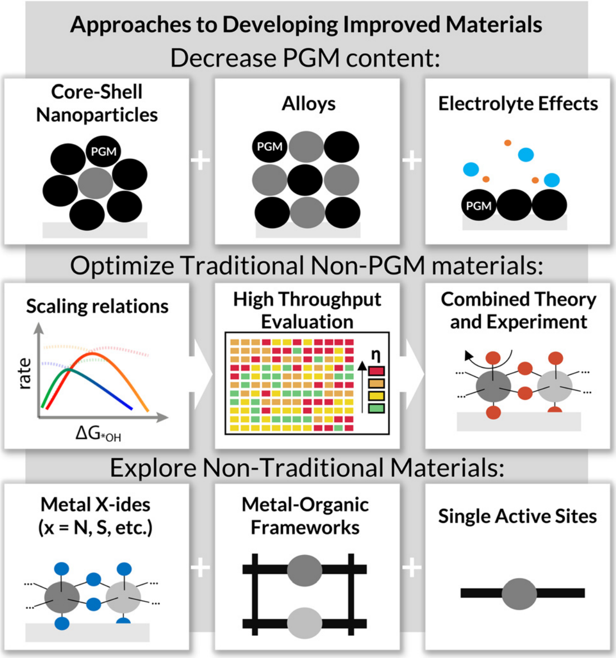


Fig. 2 ORR catalysts are primarily engineered by either tuning covalent interactions or binding of different species to change activity by modifying transition state energies and thermodynamic binding energies or tuning proton activity and dynamics to change ORR activity by changing proton transfer barriers. Three initial avenues for performance-oriented ORR engineering focused on (1) decreasing PGM content (top), (2) optimizing traditional materials *e.g.* metal oxides, *via* theoretical approaches, high-throughput evaluations, and combined theory-experimental efforts (middle), and (3) exploring non-traditional ORR materials (bottom).

2.1 Decrease PGM content

Three promising strategies for decreasing PGM content are (1) pairing earth-abundant metals with PGMs to create core–shell particles, (2) pairing earth-abundant metals with PGMs to create new alloys and (3) modulating the electrolyte environment to enhance the PGM performance. We now discuss examples of these three strategies in turn.

The core–shell nanoparticle (CS NP) architecture provides several advantages over pure Pt catalysts, including increased sinter resistance of Pt,[39] decreased catalyst lifetime cost,[40] and tunable adsorbate energies of PGMs.[41,42] Adsorbate energies on CS NP catalysts are highly dependent on bonding interactions between the core and shell materials. CS NPs with a uniform particle size distribution between 6–8 nm and tunable shell thickness can be synthesized through a self-assembly process of noble metals on a transition metal carbide core. The binding energy may be tuned through modulating the transition metal identity and nitridating the CS NPs to create a nitride core.[43] TRI consortium researchers have studied the activity and stability of core–shell catalysts composed of Pt/TiWC and Pt/TiWN for ORR (Fig. 3A). These studies indicate a ∼30–40% enhancement in specific activity of the Pt/TiWC relative to a conventional Pt/C catalyst. Similarly, Pt/TiWC showed an improvement in stability as well, losing 14% of its initial specific activity relative to 22% for Pt/C after accelerated stress testing (AST).[36]

Alloying is another powerful strategy to improve intrinsic electrocatalytic activity and lower catalyst cost by decreasing precious metal content, seminal examples of which have been demonstrated for Pt alloy systems.[44,45] State-of-the-art Pt alloy catalysts with Ni[35] and Co[19] have outperformed targets for light-duty vehicle activity and stability. PtCo catalysts are now commercialized in the Toyota Mirai.[10] It is well known that the non-precious components of these alloys dissolve over time in PEMFCs.[46] Outside of proton exchange membrane FCs, alloying is also a promising strategy for decreasing PGM content in anion exchange membrane (AEM) FCs. Due to their alkaline environment, AEM FCs have the potential to stabilize a larger range of materials, including non-PGMs. Combined efforts from the TRI consortium have refined the approach of alloy engineering by demonstrating significant ORR activity enhancements on Ag–Cu,[47] Ag–Mn,[48] and Ag–Pd[37] alloys, in 0.1 M KOH, compared to their parent materials. Ag–Pd alloys were systematically synthesized using the same e-beam PVD co-deposition technique resulting in stable electrocatalysts with state-of-the-art intrinsic ORR activities (Fig. 3B).[37] Up to 5-fold ORR activity enhancements, at 0.9 V *vs.* RHE, over pure Pd were seen for Ag–Pd alloys with Pd surface content greater than or equal to 50 at%, with $Ag_{0.1}Pd_{0.9}$ demonstrating the greatest enhancement.[37] Ligand effects arising from the electronic interactions of Ag and Pd in the alloys with medium-to-high Pd content were shown to tune the adsorption energies of oxygen intermediates on Pd–Pd sites resulting in the observed enhanced ORR kinetics.[37]

While there is substantial effort in optimizing the catalyst composition, the environment also plays a role in catalyst performance, particularly in reducing proton-transfer barriers. In one study addressing how electrolytes influence kinetics, consortium researchers found descriptors for the kinetic effects that various ionic liquids have on ORR catalysis. More specifically, as shown in Fig. 3C, a strong volcano relationship between pK_a and specific activity of both Au and Pt ORR activity, further evidenced by interfacially-sensitive spectroscopy, demonstrates that the structure of hydrogen bonds at the electrode–ionic liquid interface plays a critical and quantifiable role in ORR kinetics.[38] Furthermore, while typically considered inert, electrolyte anions (in acid) or cations (in base) in the electrode double-layer can interact with the catalyst and modulate activity through competitive adsorption (blocking active sites and modulations of the electronic structure) and near-surface electronic effects. In a different study on electrolyte effects, consortium researchers surveyed planar metal Ag and Pd surfaces to better understand the role that the anion or cation could play on ORR activity, determining that electrolytic species affect observed catalytic activity because of variable competitive physi- and chemisorption, varying intermolecular interactions between aqueous species and adsorbate, and near-surface effects on, *e.g.*, the electric fields present at the electrolyte–electrode interface.[49]

These highlighted studies demonstrate the importance of understanding the role that geometry and electronic structure play in catalytic activity and underscore the opportunities for tuning the electrolyte microenvironment. Together they demonstrate the ever-growing number of important factors when designing the optimal catalyst. However, due to the in-depth nature of this research, each study was only able to evaluate one class of material or environment. This begets the question of how catalyst morphology, composition, and microenvironment combinations can be pinpointed without having to do an exhaustive evaluation of each system.

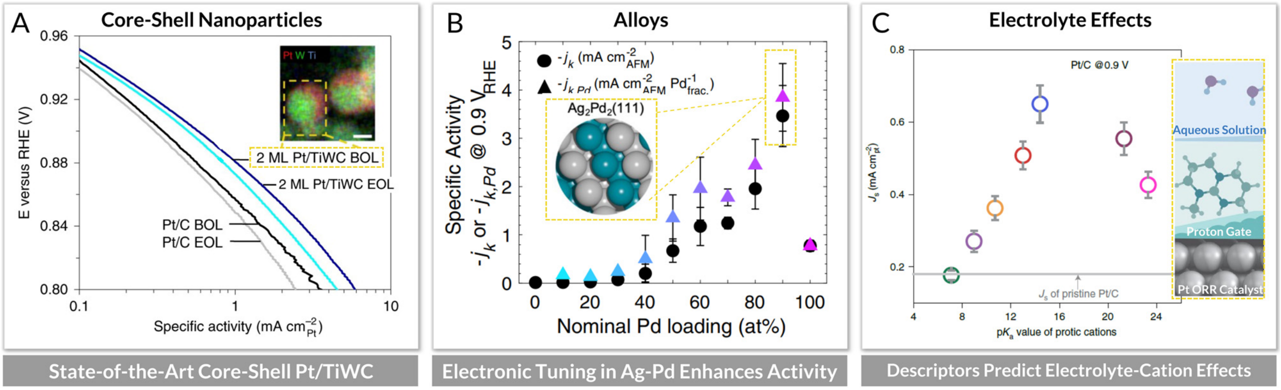


Fig. 3 (A) Core–shell nanoparticles of Pt/TiWC demonstrating improved activity and comparable stability to Pt/C in acid,[36] (B) alloys of Ag–Pd exhibit high specific activity at 90% Pd, 10% Ag composition relative to pure Pd in base,[37] (C) pK_a of interfacial ionic liquids correlates with activity enhancement observed on Pt/C in acid.[38]

2.2 Optimize traditional non-PGM materials

For fundamental studies aimed at understanding non-PGM materials, primarily transition metal oxides (TMOs), TRI consortium researchers adopted strategies which fall primarily into three themes (see Fig. 4). These are (1) deriving scaling relations to understand activity trends and fundamental limitations on the maximum activity of TMOs, (2) conducting high-throughput experiments to evaluate hypotheses for such trends and fundamental limitations, and (3) combining experiment and theory to build an understanding of transition metal oxide activity and stability for select cases.

TMOs are commonly explored in studies of the ORR, and various metal oxides are known to be stable under acidic[50–58] as well as alkaline reaction conditions, with much higher ORR

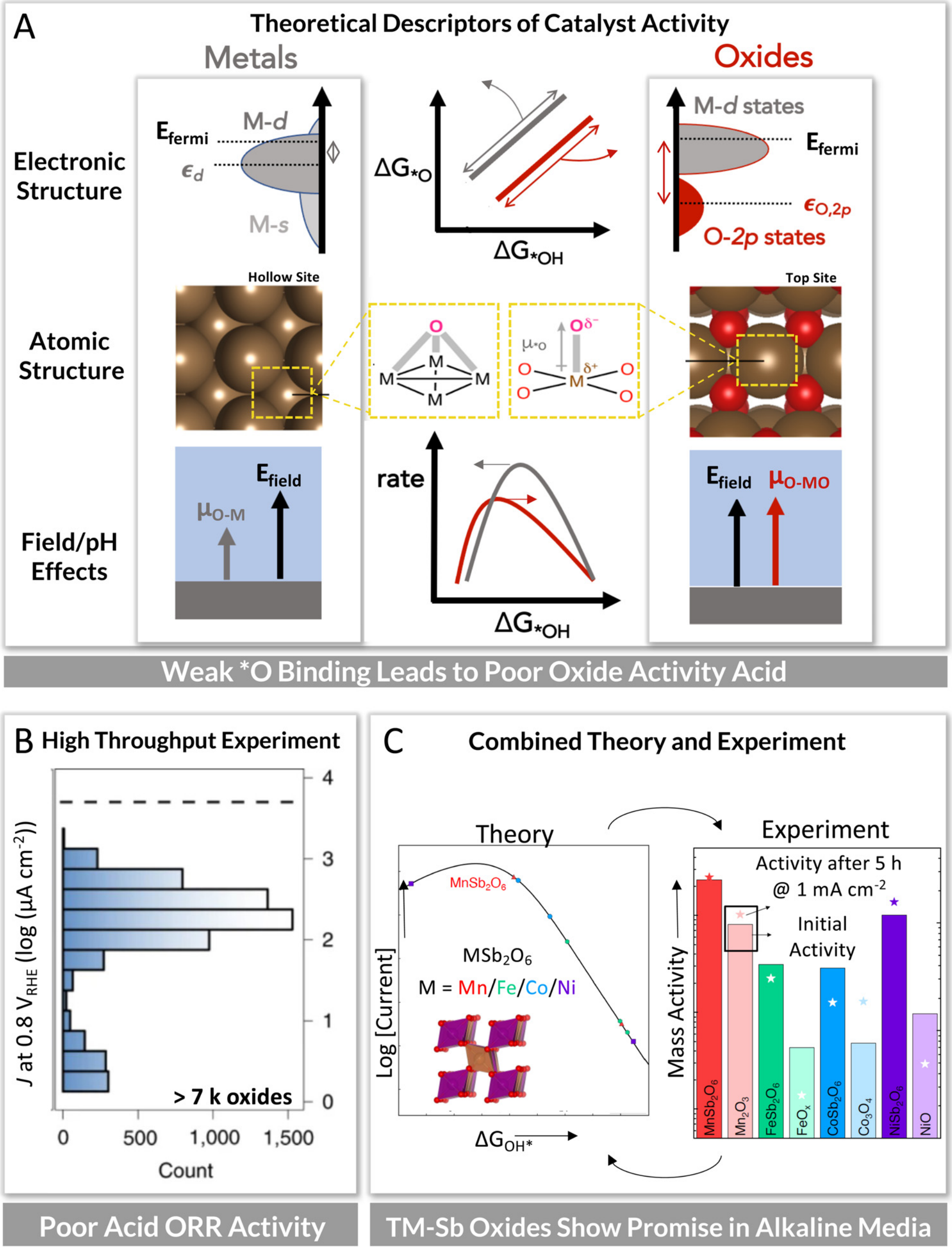


Fig. 4 Three themes in the study of transition metal oxides, conventional non-PGM catalysts. In (A), we outline the theory that rationalizes metal *vs.* oxide catalysis as a function of electronic structure, atomic structure, and pH effects from the electrolyte–electrode interfacial electric field. d-projected (metals) and p-projected (oxides) density of states (DOS) parameters explain variations within material classes along their respective metal (gray) and metal-oxide (red) scaling lines, while adsorption geometry explains the difference in scaling line intercepts and interfacial dipoles resulting from this geometry explain high variations in acid/alkaline performance of TMOs. In (B) a histogram of measured current densities on over 7000 distinct compositions of transition metal oxides is shown (blue bars) relative to the value for Pt (black dashed line), demonstrating how the theory of poor oxide performance relative to metals applies to a broad set of materials.[59] In (C), we show the results of a combined experiment and theory study how scaling relations and electrochemical microkinetic modeling can be used to optimize the performance of an acid-stable antimonate TMO according to the theoretical principles in (A).[60]

performance observed to-date at alkaline pHs. However, even the best TMO catalysts are far less active than Pt-based electrocatalysts both in acid and alkaline media. To rationalize the performance of TMOs and PGM systems, TRI consortium researchers used scaling relations and volcano analysis to identify key characteristics of TMOs and PGM catalysts to explain their behavior.

Correlated variations in *O and *OH adsorption energy within the metals, which gives rise to variations in catalytic activity and a theoretical maximum of ORR catalyst activity, can be explained by a well-known underlying descriptor, the d-band center.[7,61] Through further scaling relations, along with understanding of such a descriptor for oxide adsorption, OER and ORR activity has been more recently identified as the center of the p-projected density of states.[62,63] TRI consortium researchers identified how this descriptor generalizes to predict the behavior of not only oxygen adsorbates (and therefore ORR), but O-vacancy formation and a number of other molecular adsorption processes, which enables design of optimal TMO catalysts from an electronic structure perspective.[64] Design principles rationalized *via* the inductive effect and its impact on electronic structure have also been derived by consortium researchers to explain how metal substitution impacts electronic structure, and therefore oxygen adsorption *via* the aforementioned principles.[65] However, explaining why TMOs are generally worse in both acid and alkaline media, or why there are variations in performance between pH regimes that are more severe for TMOs, required further comparative studies of the two material classes.

First, the differences between oxygen bonding geometry on TMO *vs.* metal surfaces plays a key role. On many TMO surfaces, the atomic oxygen binds to the metal-atop sites, which are the only available sites on an oxide surface (Fig. 4a). For metals, stronger O* bonds in hollow sites not present in TMOs facilitate the breaking of O–OH bonds in the most common rate-limiting step for ORR. This structural feature may prevent some TMOs from achieving higher ORR activity than metal catalysts. Combined with the observation that the metals whose surfaces are oxidized the least under ORR conditions are precious metals, this observation poses substantial challenges for the discovery of effective non-precious metal ORR catalysts and focuses efforts to identify TMOs with O–OH binding energetics that deviate from the trends established with previously-studied TMOs.[59]

The second effect identified by TRI consortium researchers that distinguishes metal catalysts from TMOs addresses the pH-dependence. Local interfacial electric field effects (arising due to pH differences from the point of zero charge) influence metal–oxygen bonds (*O) in TMOs more significantly than on metals. The pH dependencies of weak-binding metal ORR catalysts on the RHE scale can be rationalized as originating from electric field effects.[66,67] More specifically, on the RHE scale, local electric fields at the interface are more positive in acidic electrolytes and *vice versa* for alkaline. For TMOs, the weaker (and longer) M–O bonds have larger (and more positive) dipole moments than on the metal surfaces. Therefore, M–O bonds on oxides are stabilized more at higher pHs (*i.e.* more negative fields) due to a stronger interaction between the adsorbate and the local electric fields at the electrode–electrolyte interface. Furthermore, this can be accounted for in microkinetic models, which use electrochemical transition state scaling laws that take field effects into account. Rates computed from these models with the field and structural effects for TMOs and metals demonstrate the clear distinction between the two classes of materials. The models which account for field and structural effects are not limited to TMOs, and may be useful in further studies to engineer not only bulk materials and their surfaces, but interface and electrolyte conditions which promote ORR catalysis.[59]

Providing further evidence for this theory, work in the consortium revealed that these limitations hold in a large and near-comprehensive composition space of TMOs. More specifically, over 7000 unique TMO catalyst compositions in chemical spaces containing up to 6 distinct elements sampled from a total of 15 elements were surveyed for activity using a high-throughput scanning-droplet electrochemical cell. From this dataset, shown in a histogram in Fig. 3b, even the most active TMOs have measured current densities near an order of magnitude smaller than Pt, providing evidence that limitations on TMO surfaces predicted by theory, either from restricted adsorbate binding geometries or electrolyte interactions, have broad applicability.[59]

However, TMO catalysts remain significantly cheaper in many cases and potentially more durable than metals and metal alloys, and TRI consortium researchers have also demonstrated how collaborations between theory and experiment can design and rationalize the behavior of new catalysts with optimal activity and engineered durability. Inspired by experiment–theory collaborations prior to the consortium that revealed acid-stable antimonates for the oxygen evolution (OER) reaction,[68] the activity behavior of transition metal antimonates was further explored for the ORR using both the aforementioned microkinetic modeling techniques and a framework for more accurately predicting electrochemical stability using the SCAN[69] DFT functional. In that work,[60] experimental results for the most active alkaline catalyst composition (specifically, $MnSb_2O_6$) as well as trends in the loss of ORR activity in acid were accurately predicted by theory, demonstrating the power of the predictive tools for guiding future explorations into new material classes and the persistent relevance of experiment–theory collaboration to understanding catalysts more generally.

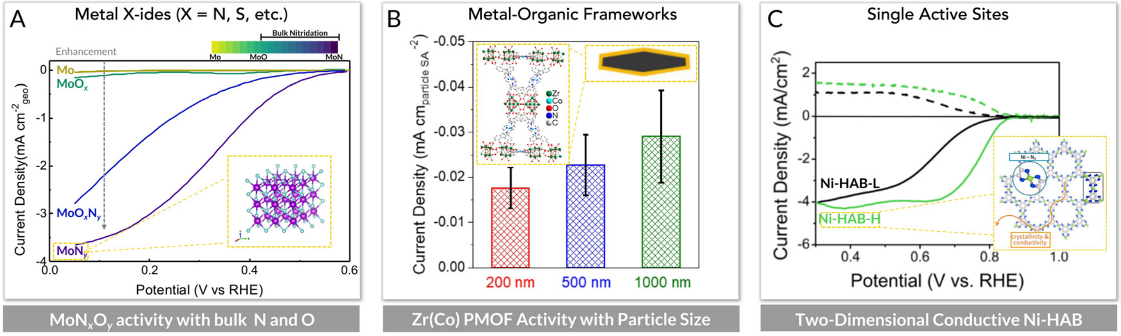
The future prospects for a precious-metal-free TMO catalyst in acidic conditions hinge upon the identification of an active and stable catalyst that either breaks the scaling relationships underlying the predicted limiting activity or operates near the activity limit with subsequent engineering of the active site density to achieve device-relevant current densities. A recent breakthrough aligned with this latter strategy has been demonstrated by consortium researchers with a $CoSb_2O_6$ catalyst for the acidic ORR.[70] By using an electrolyte recirculation cell to enable equilibration of the catalyst with dissolved metals in the electrolyte, $CoSb_2O_6$ was found to undergo 4 hours of catalyst conditioning after which the ORR activity and dissolved metals concentrations equilibrated. Subsequent measurement for an additional 20 hours revealed a very low corrosion rate of 0.04 nm $hour^{-1}$ with consistent activity of -0.17 mA cm^{-2} at 0.7 V *vs.* RHE. This current density is not competitive with Pt but is near the predicted activity limit for TMOs in acid. Computational modeling of the operational catalyst surface revealed that partial H coverage of the catalyst surface results in the formation of an Sb-based active site with a near-optimal HO* binding free energy of 0.49 eV. Collectively, the experience with TMO catalyst discovery has elucidated the substantial challenges that remain to replace Pt in acidic fuel cells, although discovery of conditioned TMO catalysts like $CoSb_2O_6$ provides strategies for optimizing oxide materials.

2.3 Explore non-traditional materials

The expansion of candidate materials beyond the current suite of promising non-PGM catalysts is a challenging but worthwhile task. One attractive target, with a clear theoretical basis, are catalysts that can break known scaling relations. In order to expand the space of potential new classes of ORR catalysts, our consortium explored three strategies: (1) metal X-ides, (2) metal–organic frameworks (MOFs), and (3) single site catalysts. Developing materials for the explicit purpose of breaking scaling relations, however, requires a deep fundamental understanding of the material active site.[8] Unfortunately, in many cases, the stability of these materials, *e.g.* metal–organic frameworks,[71,72] is not maintained throughout testing. While stability will be discussed more thoroughly in Section 3, it is notable that any fundamental study of non-traditional material must be accompanied by clear material stability analyses to construct structure–composition–activity relationships.

Exploring the x-ide systems, research efforts have focused on understanding the performance of transition metal nitride catalysts for the ORR. Thin film Ni- and Mo-nitride catalysts were found to show promising ORR performance in acidic conditions.[76,77] Oxygen content and surface oxidation were found to be significant indicators of activity and stability for both systems and were tunable based on the potential cycling conditions (Fig. 5A). Pourbaix analysis indicates the thermodynamic favorability of oxide and/or oxynitride species in the ORR potential window in acidic and alkaline conditions. The mutability of the nitride surfaces as well as the many possible surface reorganizations make these catalysts difficult to model with current theoretical methods. A theoretical study of model cobalt nitride systems found that catalysis was significantly enhanced with 1–4 monolayers of oxide on the surface of the nitride; these changes are attributed to a change in O* adsorption site from surface N to surface Co, resulting in decreased binding energy and higher overall limiting potential.[78] Although the catalyst surfaces are likely to be more complex than this core–shell model of nitride and oxide, this work demonstrates the significant impact of surface composition and structure on catalytic activity. To understand and utilize these surface transformations to enhance catalytic performance, experimental efforts must be directed towards determining the true catalyst surface, such as through in operando characterization, and theoretical methods must be developed to accurately model these surfaces.[73]

MOF catalysts are attractive due to their potential for enhancement *via* confinement. The consortium evaluated the ORR activity of the bimetallic Co/Zr-MOF, (Co)PCN222.[74] The effect of (Co)PCN222 particle size and morphology on ORR activity was probed with cyclic voltammetry on 200 nm, 500 nm, and 1000 nm catalysts. While the catalyst's performance was far below that of Pt (>200 mV), it was found that the 200 nm particles exhibited the highest activity when normalized by Co content (0.43 V *vs.* RHE). Since the low intrinsic conductivity of (Co)PCN222 makes it likely that only surface sites participate in ORR catalysis, this activity could be ascribed to the higher proportion of $Co–N_4$ active sites on the surface for smaller particle sizes. On the other hand, the 1000 nm catalyst exhibited the highest surface area-normalized activity (Fig. 4B). Although this result could indicate higher intrinsic surface activity, SEM imaging indicates aggregation of the 200 nm particles, making it likely that mechanisms such as insufficient particle-support contact and aggregation contribute to the



MoN$_x$O$_y$ activity with bulk N and O

Zr(Co) PMOF Activity with Particle Size

Two-Dimensional Conductive Ni-HAB

Fig. 5 ORR activity of (A) molybdenum (oxy)nitride thin films as a function of O and N content in 0.1 M $HClO_4$ acid electrolyte,[73] (B) Zr(Co)porphyrin metal-organic frameworks as a function of particle size in 0.1 M $HClO_4$ at 0.43 V *vs.* RHE,[74] and (C), Ni-HAB, a single-atom catalyst (SAC) in 0.1 M KOH.[75] The highest performing catalyst tested in each study is highlighted with a yellow box with its structure as an inset.

observed activities. Based on the results of this work, it is recommended that for future studies on low conductivity MOF frameworks for ORR, small particle sizes and controlled dispersion should be targeted.[79] However, it is important to note that while MOFs are very interesting from a fundamental active site perspective, without significant improvements to conductivity and stability they will struggle to hit industrially relevant performance targets.

Outside of PGM-based materials, metal–nitrogen–carbon (MNCs) catalysts have shown the most promise for translation into fuel cell configurations, and a list of such materials and their associated activity benchmarks is collected in ref. 26. More broadly, MNCs overlap with a class of materials that have isolated active sites termed single-atom catalysts (SAC), which have garnered considerable interest in recent scientific literature on ORR.[80] Our consortium has conducted theoretical studies of MNCs, demonstrating *e.g.* the effects of varying theoretical methodologies to both electric structure and solvation significantly affect the predicted overpotentials of these catalysts.[81] A further high-throughput DFT study derived scaling relations for 2-D material embedded MNCs, which lead to a volcano relationship with a peak higher than that of conventional metals.[82] Realizing SAC-type materials in the laboratory is more challenging, but a combined experimental and theoretical study yielded an instance of a unique MNC, a two-dimensional Ni-HAB, which DFT results suggest has a mechanism mediated by the Ni-containing linker near the peak of the conventional activity volcano.[75]

From these and other studies, MNCs, MOFs, and other unconventional catalyst materials seem likely to remain a promising direction for the engineering of more active catalysts, but it is also clear, both within and outside our consortium,[26] that the most significant hurdle towards their success in commercial fuel cell devices is in ensuring their long-term stability.

3. Path forward: an emphasis on electrochemical stability

While improvements in activity have largely driven the proof-of-principle catalysis research, stability is a critical figure of merit for the commercial application of novel ORR catalysts in fuel cells. For instance, in the mobility sector, FC-powered heavy duty trucks are expected to last 1 000 000 miles (or 25 000 operating hours), which is significantly higher than the 150 000 miles expected of light-duty passenger vehicles.[13] A fundamental understanding of why and how fuel cell catalysts degrade, along with more diverse accelerated stress testing that can study fuel cell lifetime will be necessary to realize fuel cell technology in commercial vehicles. For additional detail, we refer the reader to a recent review by Cullen *et al.*,[13] which explores the durability requirements of future generations of fuel cells for heavy-duty vehicles and motivates our renewed focus on the scientific questions surrounding FC catalyst stability.

Catalyst stability remains one of the major challenges in fuel cell development but is generally less studied than activity. Stability is difficult to address computationally due to the role of kinetics in stabilizing thermodynamically unfavorable phases. While metastable phases themselves can be studied, it is computationally challenging to predict which will be stable under what conditions. Furthermore, catalyst instabilities can be manifested in different ways, and different forms of stability are distinguished by the terms chemical stability, *i.e.* persistence of structure and composition in electrolyte without applied bias, and electrochemical stability, structure persistence under an applied bias voltage. Similarly there is electrocatalytic stability, or structure persistence under the conditions of catalysis, and electrocatalytic performance stability, the persistence of a measured catalytic current density or selectivity. The conflation of these properties and their underlying phenomena speaks to the need for a greater understanding of electrocatalyst stability as a whole.[72]

Moreover, in the case of electrocatalytic performance stability, phenomena underlying losses are frequently related to the properties of the support, which is typically high surface-area carbon.[83] Carbon corrosion, particularly during fuel-starvation conditions induced by FC startup, shutdown, and anode flooding can cause destruction of catalyst connectivity, collapse of the electrode pore structure, loss of hydrophobic character, and an increase of catalyst particle size.[84] Alternative supports like solid carbon, graphitized carbon, and metal oxides have shown promise in the literature,[85,86] but the atomistic understanding of the stability of these and other novel support materials, similarly to that of the stability of the active catalyst material, is still being built.

Ultimately, both catalyst development is hindered by the lack of systematic understanding of stability. Our consortium work to date on stability is summarized in Fig. 6.

3.1 Experimental stability testing

A full understanding of a catalyst's stability can require knowledge of how the catalysts' oxidation state, loading, structure, and morphology interact with the reaction process. Typically as-prepared catalysts are compared before-and-after oxygen reduction. However, once the catalyst is out of reaction conditions it is difficult to correlate any structural, compositional, or morphological changes to a particular mechanism. By understanding these changes, and the nature of the catalyst under reaction conditions, however, protocols could be developed to maximize catalyst performance without sacrificing stability. Therefore, new methodologies which make the task of characterization easier may enable a better understanding of the mechanisms affecting catalyst stability. A number of techniques have been used to probe electrocatalysts *in situ* or *in operando*, including, but not limited to, X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), in-line inductively coupled plasma mass spectrometry (ICP-MS), and ambient pressure-X-ray photoelectron spectroscopy (AP-XPS).[73,87–89] For a review of different *in situ* characterization techniques for

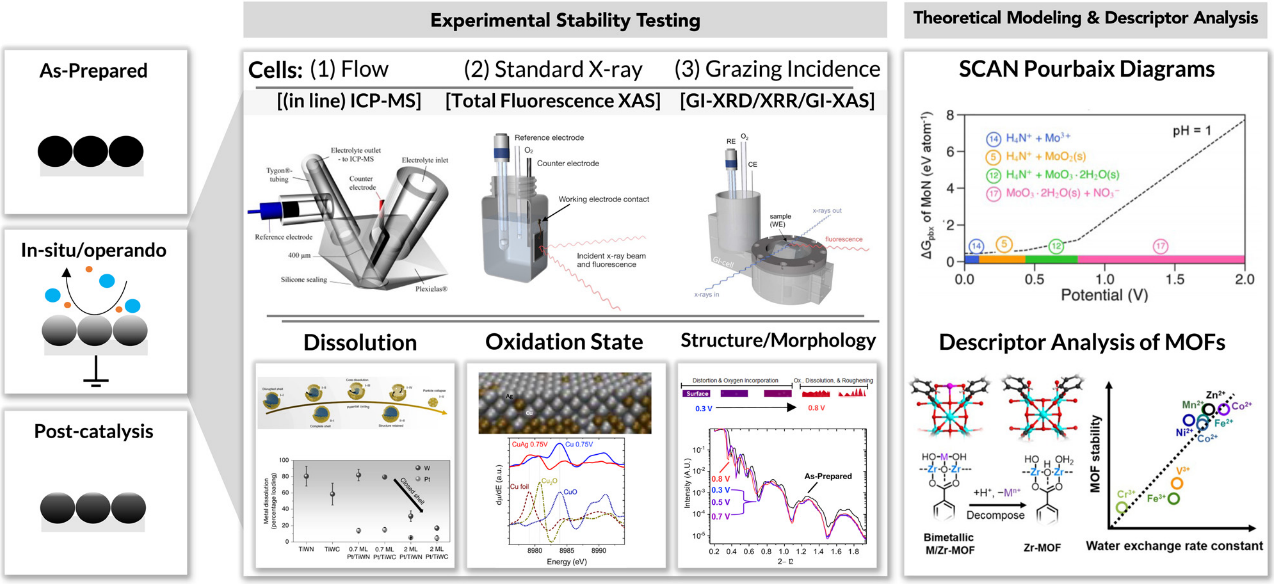


Fig. 6 Overview of stability assessments done in the TRI consortium, including those acting on as-prepared, *in situ* or *in operando*, or post-catalysis samples. Techniques include (1) ICP-MS acting on a flow-cell, revealing solution phase products from catalyst instabilities,[36,91] (2) XAS which describes oxidation-state behavior in catalyst samples,[92] and (3) grazing incidence techniques highlighting XRR, which provides information on surface roughness.[73] Theoretical frameworks for describing stability include DFT-based electrochemical thermodynamics with enhanced accuracy from the SCAN functional[73] along with descriptor analyses applied to MOFs.[93]

probing electrochemical surfaces we refer to recent work by Pishgar *et al.*[90]

There are two major challenges of performing *in operando* catalysis experiments: achieving surface sensitivity with the measurement techniques, which may traditionally be used for measurements of the bulk/subsurface, and creating realistic reaction conditions and rates in the operando cell. The latter condition is critical for the ORR, as the major limitation for *operando* experiments is enabling sufficient mass transport of O_2 to the catalyst.

ICP-MS is a commonly used technique for determining the mass of metal species in a sample. Traditionally, ICP-MS has been used for electrocatalysis to measure mass loading before and after testing, as well as to measure the dissolved metal content in the electrolyte.[79,94] While useful for understanding overall stability, this approach does not give detailed information about the time- or condition-dependence of the mass loss or gain. To address this deficiency, aliquots can be taken from the electrolyte over the course of the experiment to construct a time series of dissolution. This time series can provide understanding of how potential-cycling and constant potential or current experiments affect dissolution.[77,95] To achieve good time resolution an in-line ICP-MS is needed, which can provide time resolution up to 0.1 ms.[96] By correlating the potentiostat time to the ICP-MS time, dissolution down to the parts per trillion (ppt) level can be measured as a function of the reaction conditions. While relatively new, in-line ICP-MS has been applied successfully to a number of catalyst systems, including Pt and Fe–N–C catalysts for the ORR and Ir-based catalysts for the OER.[97–100] To further understand the promising core–shell nanoparticles studied by consortium researchers (Fig. 3a), *in situ* studies of the Pt/TiWC CS NPs were conducted in a scanning flow cell where Pt/TiWC and Pt/TiWN CS NPs with 2 monolayers (ML) of Pt coverage showed enhanced stability, losing only 20% and 30% of W after galvanostatic measurements, relative to the 60–80% loss from their Pt-free counterparts.[36] This disproportionate dissolution indicated that the performance losses observed for CS NPs were all due to the dissolution of CS NP particles with imperfect Pt surface coverage, suggesting that the stability of Pt/TiWC catalysts could be improved with enhanced synthetic methods to achieve complete coverage of the labile TiWC cores.[36] In addition to achieving complete Pt coverage, the stability of CS NP catalysts could be optimized for ORR in future work through the incorporation of more stable core materials[101] or additional phases such as phosphides.[102]

X-Ray absorption spectroscopy (XAS) is an element-sensitive spectroscopic technique that can measure features of the absorbing element's local environment, including coordination number, oxidation state, and nearest-neighbor distribution.[103] For XAS, many (dependent on the edge energy) experiments can be performed in a liquid electrochemical cell with bubbled O_2 akin to standard rotating disk electrode (RDE) testing, although the photon path length through the electrolyte must be minimized. Surface sensitivity is desirable because catalysis, and most catalyst changes, occur at the surface. To effectively characterize the active surface, contributions from the bulk must be minimized. One way to minimize bulk effects is to use very thin films, such that the contribution from the surface dominates the total signal. Work in the consortium utilized this strategy to investigate copper-silver ORR catalysts using *in situ* Cu K-edge and Ag L-edge XAS.[92] The thin film (5 nm) catalysts, deposited on 8 micron-thick pyrolyzed Kapton, were back-illuminated in a bottle cell configuration to avoid x-ray attenuation in the electrolyte. Seeking to understand the improved performance of the CuAg alloy, as well as the hysteresis observed in cyclic voltammetry, XAS measurements were made as a function of pre-conditioning and applied potential. Both the improved activity and the hysteresis of the CuAg alloy are found to correspond to the oxidation state of Cu, indicating that ORR activity is highly dependent on the electronic structure of the Cu active site.

In cases where surface sensitivity is required and it is necessary to decrease signal contribution from the bulk, there are several *in situ* grazing incidence (GI) techniques, which utilize shallow angle X-rays to decrease the penetration depth within the film. A combined-technique *in situ* study was recently used to probe the potential-dependent behavior of molybdenum (oxy)nitride thin films (30 nm).[73] In *ex situ* experiments, ORR performance was found to be improved through pre-conditioning with exposure to oxidizing potentials. Using *in situ* GI-XAS and XRR to probe the Mo K-edge and surface morphology, respectively, exposure to moderately oxidizing potentials was found to result in local ligand distortion, O incorporation, and amorphization at the catalyst surface and no surface roughening, indicating that the active surface of the nitride at ORR-relevant potentials is likely an oxynitride in character. Exposure to more oxidizing potentials was found to destabilize the catalyst, leading to dissolution, roughening and O incorporation into the bulk of the film, indicating the trade-off between activity and stability in these highly tunable non-precious metal catalysts.

Altogether, we have touched on only a handful of useful *in situ* experimental techniques for probing electrochemical stability. Many of these techniques are cumbersome and require access to high energy X-rays (synchrotrons), specialty equipment (*e.g.* in-line ICP), and deliberate cell design (GI-techniques). However, while our consortium has leveraged different aspects of our academic, national laboratory, and industry collaboration to get a holistic picture of the stability of many catalyst systems, we reiterate that these techniques are available to the community at large and hope that our overview encourages further partnership between national labs, academics, and industry in order to address the issue of catalyst stability. User facilities are application-based use and collaborations can be fostered to answer these pressing questions. Even with these techniques, however, there are questions on the atomistic level that remain outside of current experiment capability and can only be approached with theoretical modeling and descriptor analysis.

3.2 Theoretical modeling and descriptor analysis

Improved theoretical modeling allows for better prediction and understanding of the ORR and its catalysts. In addition, trends for catalytic properties with respect to descriptors like adsorption energies, pK_a, d-band or p-band filling, and others derived either from theory or chemical intuition can rationalize catalyst behavior across a range of materials. Consortium researchers have used and developed new theoretical tools and descriptor-based models that can assist in predictions, design, and understanding of more stable catalysts which we highlight in this section.

For solid inorganic materials like metals, oxides, sulfides, and nitrides, high-throughput DFT and the dissemination of its associated datasets has enabled researchers to access and use information on phase behavior to construct maps of material stability. The Pourbaix diagram has long been an indispensable tool in predicting phase behavior of materials under specific electrochemical conditions, and DFT data has been used to create Pourbaix diagrams to predict the stability of new materials in the past decade.[104,105] Consortium researchers have achieved two major milestones in DFT-informed Pourbaix diagrams. The first milestone involves the improvement of the algorithms used to preprocess materials data and construct the diagram itself, which previously involved exhaustively searching mixture candidates in order to populate the possible phases of the Pourbaix diagram. Using a combination of physical reasoning about which phase mixtures may be present and efficient algorithms for convex hull determination, consortium researchers devised a method, implemented in the open-source community code pymatgen,[106] to generate Pourbaix diagrams of arbitrary elemental complexity. With this method, phase diagrams which previously would have taken years may be constructed in seconds.[107]

The second milestone is using more accurate DFT functionals which has endowed Pourbaix diagrams with significantly increased accuracy in both qualitative and quantitative predictions of material stability. These SCAN[69]-based Pourbaix diagrams address prior challenges in modeling compounds other than oxides, *e.g.* sulfides, phosphides, and nitrides, which suffered from systemic deficiencies in previously used functionals.[108] In concert, these two advances have made accurate and fast determination of the stability of any given material in electrochemical conditions possible. With the advent of high-throughput capabilities for SCAN-based DFT simulations, Pourbaix analysis can support our exploration of novel materials spaces in a powerful new way.

Generating high-throughput bulk thermochemistry data for metal–organic frameworks from DFT, is still a significant challenge computationally, and thus MOFs are not amenable to aggregated Pourbaix analysis. However, descriptor-based analysis *e.g.* of the electronic structure of MOF constituents has yielded insights into their stability. More specifically, TRI consortium researchers systematically analyzed the stability of heterobimetallic M/Zr-MOFs (M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) in aqueous systems.[93] The bimetallic framework employed in this study allowed the effect of metal cations on stability to be decoupled from related factors such as pore size and coordination geometry to guide MOF design strategies. In this study, the stability was probed by incubating MOFs in aqueous solutions of varying pH for 1 hour and analyzing the resulting composition through ICP-optical emission spectroscopy (ICP-OES). The parent Zr-MOF framework provides the lower and upper pH bounds of the stability window as pH 1–11, where at more alkaline pHs the organic linker tends to leach out and at more acidic pHs the Zr^{4+} begins to leach. In general, it was found that the higher the oxidation state of the metal heteroatom, the greater the stability of the MOF; this trend is ascribed to the increasing strength of the labile M–O bonds with increasing valency. With this mechanism in mind, it was found that the water exchange rate constant (k_{ex}) of metal cations is an appropriate descriptor of the derivative MOF stability. This general finding can be used to design stable MOF frameworks for a variety of applications, including ORR.

While descriptor-based and physical frameworks for understanding and predicting catalyst stability will undoubtedly continue to be valuable, there is also an exciting opportunity to develop new models and decision-making strategies emerging in science. Future research into the ORR will likely benefit by leveraging new techniques in machine learning and artificial intelligence (AI), which we discuss in the following section.

4. New frontiers: accelerating ORR catalysis research with artificial intelligence

As shown in Section 2, non-traditional beyond-Pt materials have not yet approached Pt-like performance. The combination of factors that make an effective catalyst are often inversely correlated or impose fundamental limits on maximum ORR activity. The entire space of experiments on ORR catalysts involve innumerable combinations of compositions, structures, electrolytes, and a number of other factors. Each study brings insight that might lead to a better material, but fully examining each possibility is not practical and requires significant effort to extract principles that may be transferred to other systems. Furthermore, the *in operando* stability analyses suggested in Section 3 are vital, but on their own only offer individual pieces of a large puzzle. Therefore, if we are to accelerate the research process by accurately predicting optimal material combinations and stability, it is vital that we transition to a mode of research that can more efficiently predict the most important interactions between material properties and functionality. Realizing this paradigm shift hinges not only on improved experiments and theories, but on better acquisition and use of catalysis data. In this section, we highlight how tools of modern data science and AI can be combined with ongoing experimental and physics-based studies as we seek to develop materials that go beyond current activity limits and to understand how and why different materials degrade in fuel cells.

In our consortium, we have begun the development of systems that can assist in scientific decision-making for research into the ORR. The general capabilities of these tools shown in Fig. 7 are to (1) provide a software ecosystem to support improved data and machine-learning predictions,[109,110] (2) facilitate the process of material discovery and synthesis,[111,112] and (3) automate and enhance analysis techniques used to identify active sites, map new phases, and assess catalyst stability.[113] In addition to the ongoing development of the tools themselves, we plan to begin using them specifically to address the durability challenges in ORR outlined in Section 3.

4.1 Data and machine learning

In working with high-throughput experimental data shown in the TMO results from Section 2, we found there were practical issues handling the large volume of data. Every piece of information from the synthesis, processing, treatment, and experimental processes associated with a final measurement can be valuable data, but a complete history is challenging to collect even for a single sample. In order to more effectively manage and query this data to create an understanding of the evolution of a single sample over time, we developed a data architecture to completely capture the process history of individual samples by associating processes acting on samples as events in a graph database. This framework, dubbed the event-sourced architecture for materials provenance (ESAMP),[110] makes it easier to create a digital record of the provenance associated with either a laboratory or computational experiment. ESAMP ensures that the data follows FAIR[114] guiding principles and the underlying framework that is used to push data into an ESAMP architecture is flexible enough to be easily modified in accordance with changes to scientific assumptions. ESAMP's ability to completely capture the process provenance of a material enables it to be used for transparent curation of machine learning data *via* human or machine generated rules that assign individual processes as state changing (or not). Because many different processes – from treatment to electrochemical measurement to storage and transportation – can affect the state of a material, records of the full provenance may allow for discovery of which processes change the state of a material. In the future, we anticipate the ESAMP architecture to be useful for efficient linking of multiple datasets, theory-experiment integration, and machine learning for identification of experimental workflows. For example, by enabling linkage of characterization and electrochemical treatment experiments over long periods of time, it may be easier to determine how and why the state of a sample changes, therefore shedding light on stability trends.

In concert with this data ecosystem, ML has the capability to power autonomous systems which can recommend or even control which new experiments are selected based on past results. To refine this capability, TRI has developed methods which quantify the effectiveness of active learning processes by simulating the methods on past datasets. More specifically, using high-throughput data of measured ORR overpotentials,[115] TRI consortium researchers developed metrics by which to judge how much a given active learning model and acquisition strategy accelerated the rate at which the best catalysts of a given dataset are discovered or the rate at which the model improved, *i.e.* the understanding of the relationship between material composition and ORR rate.[116] Further, in a separate project, this active learning simulation capability was formalized, automated, and used to compare active learning strategies for acquisition of stable crystal structures from simulation and multi-fidelity acquisition of both

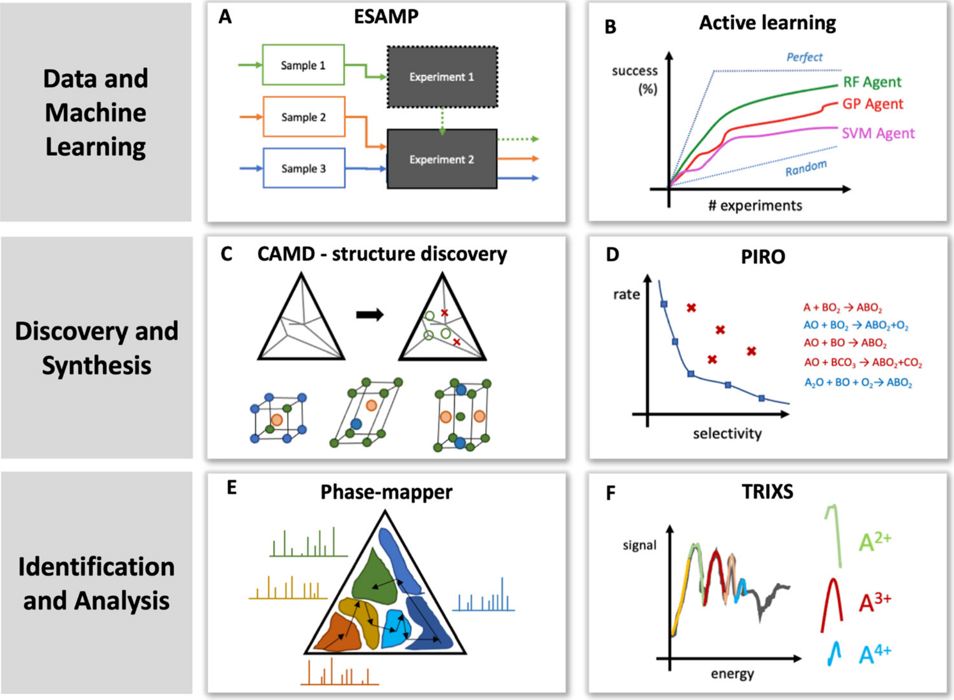


Fig. 7 New AI tools to be applied in catalysis research. ESAMP (A) can be used to organize experimental data by the state-changing events, enabling future aggregation and analysis based on the complete provenance. Active learning simulation (B) enables the simulation of "agents," in order to benchmark how efficiently they explore new chemistries, structures, or experimental process parameters in order to discover new catalysts with the best figures of merit. CAMD (C) is an autonomous system for efficiently finding new crystal structures predicted to be stable by DFT, and can arm researchers with knowledge of the predicted phase diagram and new potentially discoverable phases. PIRO (D) generates and organizes synthesis recipes for target crystal structures by sets of known precursors, and predicts the pareto-optimal set of synthesis recipes from DFT-based thermochemistry according to predicted rate and selectivity metrics. Phase-mapper (E) assists in structural characterization, predicting the most efficient next experiment for determining the distinct phases in a given chemical space. TRIXS (F) assists in X-ray (*e.g.* XANES) characterization by featurizing experimental or simulated spectra in order to rapidly identify evidence of particular electronic structural motifs in samples.

DFT-computed and experimental band gaps from known datasets.[111,117] This approach enables the testing and optimization of agents, programmable objects which contain instructions for selecting new experiments based on past results like those used in the aforementioned active learning simulations of Rohr *et al.*[116]

Ultimately, this ability to conduct retrospectives on the decision-making process in simulations of active learning is key to ensuring our future experiments are more likely to discover more active and stable catalysts. In one consortium study, an active learning simulation was used to target nanoparticle compositions which exhibit a specific structural property of having a single interface between two phases. After being trained on known data from SEM nanoparticle micrographs, a Gaussian-process-based agent predicted 18 new compositions that were confirmed to have a single interface of 19 that were experimentally tested, including the most complex bi-phasic nanoparticle known that contained seven elements.[118]

4.2 Discovery and synthesis

With tools like ESAMP and active learning simulation, we must set out to evaluate the prospects of new hypothetical crystalline phases efficiently. CAMD's core capability is to autonomously discover new inorganic crystal structures predicted to be stable by DFT. CAMD accepts a user-selected chemical system to explore, decorating thousands of structural prototypes with the selected chemical elements, and using a combination of machine-learning predictions, thermodynamic analysis, and uncertainty quantification to select DFT simulations that are most likely to result in the prediction of a synthesizable material.[111] CAMD provides both experimentalists and theorists with a method for augmenting their knowledge of a chemistry which they have a particular interest in. After a year of continuous operation, CAMD has autonomously assessed over 3.3 million crystal structures with its autonomous agent, choosing roughly 100 000 for DFT simulation based on machine learning predictions of formation energy and synthesizability from the compositional convex hull. Of those simulated with DFT, over 25 000 new structures found in neither of the Materials Project,[119] Crystallography Open Database,[120] nor OQMD[121] were within 200 meV per atom of the convex hull, indicating their potential synthesizabillity as stable or metastable materials. An experimental discovery campaign of CAMD-predicted materials is underway, but all of the crystal structures assessed by DFT in CAMD are now publicly available for other researchers to use in their own discovery campaigns or machine learning model construction.[122] To address electrochemical stability, CAMD's core capability can be modified to search for materials which are stable on the electrochemical phase diagram, *i.e.* Pourbaix diagram, rather than the compositional phase diagram. This capability is also the subject of ongoing development. Ideally, results of CAMD's autonomous exploration can help us identify the most promising new chemistries to explore and structures to attempt to synthesize based on theoretical data. However, there remains a challenge of providing explicit guidance on synthesis of hypothesized materials.

To begin addressing the challenge of synthesizing a crystal structure predicted from DFT, TRI developed a tool that predicts the optimal synthesis routes for inorganic crystalline materials using a combination of machine learning, thermodynamics, and classical nucleation theory. Termed "piro", this open source software package[123] recommends reagents for a given crystal structure at a given temperature and pressure. More specifically, these recommendations are those precursor materials which are optimal in terms of trade-offs between reaction rate (or kinetic barrier height) and the number of potential parasitic reactions determined from the phase diagram. Using piro, exploratory syntheses of novel materials can be planned on a "map" that shows which reagent precursors should be best in terms of yield rate and selectivity.[112] We note that validation of forward prediction of piro routes is in progress, but retrospective analysis of $LiCoO_2$, $BaTiO_3$, YCBO, and a number of other solid materials suggests that it provides not only accurate predictions, but explanatory power for success or failure since it describes synthesis in physical terms. Piro helps prospective synthesis researchers understand whether solid-state syntheses fail because the target phase cannot nucleate quickly enough or because phase competition consumes precursors towards an undesired product.

We note also that advances in natural language processing on the materials science literature within[124–126] and outside[127,128] of our consortium have resulted in valuable capabilities to extract and curate known synthesis recipes and to represent materials, applications, and various other named entities in the literature in a powerful new way. Our principal consortium effort, piro, differs from those in NLP in focusing on a physical basis for synthesis, but there may be opportunities to combine knowledge from literature data mining with physics-based theories of inorganic synthesis to leverage both kinds of knowledge. Ideally, such methods should also be adaptive to feedback from new synthesis successes and failures, particularly since there are very few examples of the latter in the literature.

4.3 Analysis

Lastly, novel machine learning techniques have the power to help us more quickly and accurately characterize the new materials we make, both in the AI-powered case and in more traditional research processes. One key capability to complement the high-throughput synthesis methods that produce spatially varying fractions of thin-film material compositions is to efficiently map phase behavior. TRI consortium members developed a tool that automates the analysis of X-ray diffraction data to generate phase diagrams. The phase mapper tool ingests new XRD patterns at successive points and uses constrained non-negative matrix factorization in order to help researchers connect structural characterization to the theoretical composition space of phase behavior.[129] This search strategy, powered by Deep Reasoning Networks (DRNets), was used to algorithmically solve the complex Bi–Cu–V–O phase diagram, which contains materials promising for photoelectrochemical water splitting. The phase mapper, which iteratively ingested XRD patterns to distinguish phases and recommend each new experiment, revealed 19 phase regions, each corresponding to a distinct combination of 12 crystal structure phases containing Bi, Cu, V, and O.[130] In the future, phase mapping may facilitate the exploration of both known and new chemical spaces to assist in synthesis, recommend experiments, and help researchers clarify structure–property relationships for ORR catalyst activity and stability.

Similarly, coupling to the aforementioned advances in XAS, a consortium effort to analyze output of large XANES data generated using FEFF,[131] an X-ray spectroscopy simulation software, demonstrated that coordination number, bader charge, and mean nearest neighbor distance could be extracted from these spectra with random-forest regression (see Fig. 7F). Additional insights into the relevant features in the XAS spectra have been demonstrated as obtainable using polynomial featurization prior to random forest regression and then analyzing model-assigned feature importance.[113] Featurization using local spectral curvature after this work has now been used outside of our consortium[132] as a descriptor to resolve structural properties like coordination number, Fe–O distance, and Fe oxidation state from experimental spectra of silica-supported single-site Fe catalysts. Part of the goal of interpretable AI tools like TRIXS[133] is to build knowledge that is compatible with past human intuition. This compatibility is particularly important for X-ray studies since current technology limits experimental throughput. However, adapting characterization tools that are built initially by leveraging simulated electronic structure may require a community of researchers refining these methods well beyond our consortium, and as such openness and facile collaboration between researchers interfacing with user facilities will likely be critical.

5. Summary

In providing this overview of the past, present, and future of the TRI research consortium for ORR catalysis, we demonstrate the possibilities of inter-institutional collaboration between academia, national laboratories, and industry to address pressing scientific and engineering challenges. Further, we share our perspective to other community members so they may reuse, critique, or adapt our strategies for their own efforts. In its initial phase, our consortium has focused on investigations of conventional PGM and oxide catalysts. From these studies, we have abundant evidence that fundamental limitations on catalyst activity likely cannot be circumvented with conventional materials, as metals and metal oxides remain limited by both known activity volcano relationships and newly discovered structural and interfacial trends on *e.g.* metal oxides. However, reducing the quantity of the most expensive material components of ORR catalysts is both possible and practical for improving existing fuel cells, and can be achieved by nanostructures which preferentially expose *e.g.* Pt active sites, designing multi-functional alloys, and engineering the electrode–electrolyte interface. Furthermore, non-traditional catalyst materials like nitrides, MOFs, and SACs may hold promise of behavior outside of the limits imposed by scaling relations for metals and metal oxides, however they are dramatically limited by stability.

There are broad prospects to design more durable ORR catalysts, which are accompanied by a compelling scientific opportunity to understand electrochemical stability more holistically. Our view is that the most compelling path forward is in fundamental studies of catalyst stability. Cutting edge theoretical and experimental tools can help us characterize catalyst stability with unprecedented accuracy and resolution, and applying these tools will allow us to make headway on both engineering more stable catalysts and understanding why they are so.

Finally, we also aim to accelerate our research processes with emerging AI tools. The need for new catalysts, and new materials more generally, grows urgent, and we should leverage AI to enhance our strategies for selecting new experiments and simulations to understand and design new catalysts. Furthermore, we should enrich our research community by the continued development and sharing of these AI tools. With these tools, we aspire to meet the challenge of provisioning materials for the next generation of fuel cells, and ultimately to help power the future of human mobility.

Author contributions

J. M. G., J. H., T. F. J., J. K. N., Y. R.-L., Y. S.-H., B. S., S. K. S., and J. H. M. conceived and outlined the perspective content. M. B. S., J. H. M., L. W. and H. J. wrote Section 1 and the Summary. M. B. S., M. A., M. E. K., E. K. P., H. L., J. P., J. Z. Z., and J. M. G wrote Section 2. M. B. S., M. E. K., and J. H. M. wrote Section 3. J. H. M, S. B. T., and S. K. S. wrote Section 4. M. B. S. and J. H. M. organized and coordinated the writing and revision. All authors contributed to editing and manuscript revision.

Conflicts of interest

J. H., S. S., S. B. T., and J. H. M., have patents pending and granted related to fuel cell and materials discovery technology.

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