Molecular Iron Oxide Clusters Boost the Oxygen Reduction Reaction of Platinum Electrocatalysts at Near-Neutral pH

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Abstract: The oxygen reduction reaction (ORR) is a key energy conversion process, which is critical for the efficient operation of fuel cells and metal–air batteries. Here, we report the significant enhancement of the ORR-performance of commercial platinum-on-carbon electrocatalysts when operated in aqueous electrolyte solutions (pH 5.6), containing the polynuclear 

\[ \text{Fe}_2\left(\text{L-O}\right)_{(16)}(\text{tart})_{(10)}(\text{CH}_3\text{COO})_{(20)} \]

Mechanistic studies provide initial insights into the performance-improving role of the iron oxide cluster during ORR. Technological deployment of the system is demonstrated by incorporation into a direct formate microfluidic fuel cell (DFMFC), where major performance increases are observed when compared with reference electrolytes. The study provides the first examples of iron oxide clusters in electrochemical energy conversion and storage.

The oxygen reduction reaction (ORR) is one of the most important chemical reactions. In nature, the ORR is a cornerstone of metabolic cycles and energy exchange, while in electrochemical technologies, it is at the heart of energy conversion/storage systems such as fuel cells and metal-air batteries. ORR can significantly proceed via four proton/four electron reduction (i.e. \( \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \)) or two proton/two electron reduction (\( \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \)). The second reaction is undesirable, as the reactive peroxide species formed can oxidatively degrade sensitive components within the system.

As the ORR is a complex reaction with rather sluggish kinetics, both natural and artificial systems utilize catalysts to enhance the ORR performance. In technological settings such as fuel cells, to-date, noble metals such as platinum on carbon (Pt/C) are the most often used catalysts due to their high performance and catalytic efficiency. However, the system suffers from several drawbacks. From an economic point of view, the high costs associated with Pt metal negatively affect large-scale deployment. Also, aggregation of typical nanostructured Pt nanoparticles as well as Pt-dependent degradation of the carbon electrode are fundamental challenges for long-term operation. In addition, Pt/C does not show good ORR performance in the presence of coordinating anions (e.g. phosphate), which are present in many typical proton exchange membrane fuel cells (PEMFCs). Researchers worldwide are exploring how to overcome these limitations, and approaches range from the use of non-platinum metal ORR catalysts to the design of nanostructured Pt alloys and highly dispersed Pt particles or (sub)monolayers on non-noble metals. In addition, the use of mediators dissolved in the electrolyte has attracted significant attention. This includes redox mediators, proton-transfer mediators as well as mediators which increase \( \text{O}_2 \) solubility, leading to enhanced electrocatalytic ORR.

Here, we describe a solution-based alternative approach which facilitates enhanced ORR performance while employing widely used commercial Pt/C ORR catalysts: iron oxide polyoxometalates are introduced as redox mediators into the...
aqueous electrolyte, and experiment and theory suggest that these species enhance ORR at the electrolyte-catalyst interface.

This approach is inspired by pioneering works from the groups of Brechin, Cronin, Nyman, and Powell, and others, who discovered that high nuclearity iron oxide polyions with nuclearities ranging from Fe₈₉ to Fe₃₂₈ can be accessed and stabilized using terminal carboxylates, alkoxide, or N-donor ligands, resulting in redox-active cluster species. Note that these studies were mainly focused on the design of molecular analogues of iron oxide minerals (e.g. ferrhydrite or magnetite) and exploration of the unique magnetic properties of these clusters. In contrast, very little is known about the redox-activity or (electro-)catalytic properties of this compound class. However, metal oxide clusters are well-known redox-mediators, and have been employed in processes ranging from (photo-)electrochemical water-splitting to selective organic transformations, dye-sensitized solar cells and fuel cells.

Here, we use the iron oxo cluster K₃Na₃[Fe₈₉(M₄O)₆₋₋(L–)₋₋₋₋₋₋(CH₃COO)ₓ]ₓ2H₂O (= Fe₈₉) which was originally reported by Li, Wang and coworkers. Briefly, Fe₈₉ is composed of four identical Fe₇₇ sub-units linked by L–tartrate bridging ligands (Figure 1) which was previously studied and published by Li, Wang and co-workers. Fe₈₉ is a synergistic effect between the Pt/C catalyst and PBS solutions, we performed comparative LSV analyses of aqueous solutions containing Fe₈₉ or phosphate buffer containing aqueous solutions (50 mM) show no significant ORR activity (Figure 2c); however, the Pt/C catalyst in Fe₈₉ solution shows a distinct ORR peak at ~0.88 V vs RHE (Supporting Information, Figure S5), highlighting that the observed ORR reactivity increase shown in Figure 2a is a synergic effect between the Pt/C catalyst and Fe₈₉.

As briefly described above, the ORR performance of Pt/C in neutral phosphate-buffered aqueous solution (PBS) is affected by Pt-poisoning due to phosphate ion adsorption, so that alternative electrolytes are required, for electrochemical operation of Pt/C systems under (near-)neutral pH conditions. To provide initial insights into the performance of Fe₈₉ and PBS solutions, we performed comparative LSV analyses of aqueous solutions containing Fe₈₉ or phosphate buffer (50 mM, pH 5.6), see Figure 2d and Figure S6. These studies showed more positive onset potentials for the Fe₈₉ solution (E_onset = 0.75 V vs. RHE) compared with the phosphate solution (E_onset = 0.79 V vs. RHE). Similar trends were observed for the half-wave potentials, E_(1/2)(Fe₈₉) = 0.84 V vs. RHE, E_(1/2)(PBS) = 0.74 V vs. RHE. Also, Tafel-slope analyses of the system indicated that the Fe₈₉ solutions show lower kinetic barriers for ORR.
(106.6 mV dec^{-1}) compared with the PBS solution (136.6 mV dec^{-1}), see Supporting Information, Figure S7. Details on the superior performance of the Fe_{38} electrolyte compared with the reported PBS system are shown in the Supporting Information, Table S1.

Next, we used electrochemical impedance spectroscopy (EIS) to evaluate the charge transfer ability within the systems. As shown in Figure 2e, at open circuit potential, the Nyquist plots for both, the Fe_{38} and the PBS solution show similar overall features with a semicircle in the high-frequency region and a linear slope in the low-frequency domain. The high-frequency data show that the Fe_{38} solution features significantly lower charge-transfer resistance compared to the PBS-containing solution. In contrast, in the low-frequency domain, both Fe_{38} and PBS solutions show semi-infinite diffusion behavior, and lower ionic diffusion resistance is observed for PBS compared with Fe_{38}. This is expected, as Fe_{38} is both higher charged and significantly larger than the phosphate ions.

To study the ORR selectivity, we employed rotating ring-disk electrode-LSV (RRDE-LSV), which allows differentiation between 2-electron and 4-electron reduction of O_2. 4-electron reduction (product: H_2O) is the desired process, resulting in formation of water as product, while 2-electron reduction results in peroxide formation which can trigger component degradation (see above). Here, RRDE-LSV was employed using Pt/C-modified working electrodes operated in 50 mM Fe_{38} solution (Figure 2f). Data analysis based on the ring-current allowed us to determine the H_2O_2 yield and electron transfer number (n), which is a measure of the selectivity between 2-electron and 4-electron reduction of O_2. As shown in Figure 2f, across the potential range scanned (E = 0.45–0.60 V vs. RHE), the H_2O_2 yield is < 20 %, and H_2O_2 formation decreases with decreasing potential. This is also reflected by the electron transfer number n, which increases from n ≈ 3.7 (0.60 V) to n ≈ 3.9 (0.45 V), emphasizing the high selectivity for the 4-electron transfer.

Based on these results, we hypothesized that Fe_{38} might affect oxygen uptake and/or oxygen solubility in the aqueous electrolyte as a basis for the enhanced ORR observed. Note that gas uptake by liquids is affected by a variety of factors ranging from gas flow rate to surface tension and ionic strength of the solution. Here, we used time-resolved oxygen sensing to determine O_2-uptake by aqueous solutions of Fe_{38} and PBS (50 mM). To this end, the dissolved O_2 concentration in the aqueous solvent was recorded as a function of time using a fluorescent O_2 sensor. As shown in Figure 3a, under identical experimental conditions, faster O_2 uptake is observed for the Fe_{38} solution (12.6 ± 0.16 μmol L^{-1} s^{-1}) compared with the PBS solution (8.0 ± 0.08 μmol L^{-1} s^{-1}). Both solutions show virtually identical O_2 saturation concentrations (∼ 750 μmol L^{-1}).
These results highlight that the presence of Fe$_{28}$ in the aqueous solution improves O$_2$ uptake rates, and thus mass transfer from the gas to the liquid phase. This could be a main contributor to the enhanced ORR activity.

Next, we were interested whether the observed reactivity enhancement is specific to Fe$_{28}$ or can be triggered by any polynoxoanion. To this end, we performed comparative ORR studies using Pt/C as catalyst in aqueous solutions (50 mM) of the model polynoxoanions Na$_n$[A-PW$_{11}$O$_{39}$]$_2$H$_2$O (PW$_{11}$) and Na$_n$[A-PW$_{11}$O$_{39}$] (PW$_{11}$). As shown in Figure 3b, in all cases, RDE-LSV analyses showed poor ORR performance, thereby highlighting that the observed reactivity enhancement is a Fe$_{28}$-specific effect. We also examined whether the effect can be reproduced by simple dissolved Fe$^{III}$ species and performed ORR-studies using EDTA/Fe or L-tartarate/Fe complexes ([Fe] = 50 mM, for details see Supporting Information) as electrolyte solutions. As shown in Figure 3b, these systems also showed poor ORR performance, emphasizing that the observed ORR-enhancement is a Fe$_{28}$-specific effect. For comparison, we also synthesized two other iron-containing clusters (Na$_n$[PW$_{11}$O$_{39}$]Fe$^{III}$-($\text{H}_2\text{O}$) ) and Na$_n$[Bi$_2$Fe$_3$O$_{18}$(OH)$_{12}$(CF$_3$COO)$_{12}$](CF$_3$COO)$_{36}$H$_2$O, which can be deployed at near-neutral pH according to the literature. CV tests show virtually no enhanced ORR activity under the conditions used for Fe$_{28}$, which highlights that the observed effects are unique to the Fe$_{28}$ system (details see Supporting Information, Figures S8 and S9).

The stability and recovery of Fe$_{28}$ was studied by analyzing the material after long-time chronoamperometry (CA, $E = 0.84$ V vs RHE, $t_{CA} = 11$ h, Supporting Information, Figure S10), where a near-constant current density was observed, which highlights the robustness of the system. In contrast, the CA of Pt/C in PBS shows significantly lower stability (Supporting Information, Figure S10). The Fe$_{28}$ solutions before and after CA were studied using electrospray-ionization ion-mobility mass-spectrometry (ESI-IM-MS); these analyses showed the presence of Fe$_{28}$ before and after CA: the native Fe$_{28}$ cluster was identified by two characteristic envelopes between 900–1100 m/z (charge: 6–), and 1200–1600 m/z (charge: 5–), see Supporting Information, Figures S3 and S11. For detailed experimental and calculated peak assignments, see Supporting Information, Table S2. Post-CA analysis by ESI-IM-MS shows similar characteristic envelopes, and comparison of the experimental and simulated data verify the integrity of the Fe$_{28}$ in the post-CA solution (Figure S11, for experimental and calculated peak assignments see Table S3). Further, drying of the aqueous Fe$_{28}$ solutions under vacuum allows recovery of the compound, and pXRD (Figure S12) as well as Fourier transform infrared (FTIR) spectroscopy (Figure S13) of the dried sample indicated the structural integrity of the recovered Fe$_{28}$.

To gain insights into the performance of Fe$_{28}$ solutions in real devices, we undertook a comparative study of Fe$_{28}$ and PBS cathode solutions (50 mM) in a DFMFC (Figure 4a). As anode solutions, we employed aqueous sulfuric acid (1 M) containing HCOOH (2 M), see Figure 4. As cathode, a self-breathing Pt-functionalized gas diffusion electrode (GDE) was employed and was operated in air. Electrochemical performance analysis of the DFMFC indicated, that the system operated with Fe$_{28}$ cathode solution shows significantly higher maximum power densities (~9.5-fold increase, Figure 4b) as well as higher maximum current density (Fe$_{28}$: 66 mA cm$^{-2}$; PBS: 10 mA cm$^{-2}$, Figure 4b) compared with the PBS system. This preliminary study therefore highlights that the fundamental ORR enhancement observed in the initial experimental studies can be transferred to improving the performance of fuel cells on the cell level.

Based on these findings, we were interested to understand whether the ORR enhancement of Fe$_{28}$ is specific to Pt/C, or if it can be generalized to other ORR catalysts. Initial studies were performed using a FeCo alloy ORR catalyst synthesized according to the reported literature, and comparative LSV analyses of the catalyst in aqueous PBS or Fe$_{28}$ solution showed that the ORR-enhancing effect of Fe$_{28}$ is also observed for this system (Figure S14).

Finally, we were interested in providing initial insights into whether iron oxide polycations can in principle be ORR catalysts in their own right. To this end, we performed a series of spin-polarized density functional theory (DFT) calculations to predict the Gibbs free energy changes of the ORR process using a simplified Fe$_7$ cluster (Figure 5a). This was compared with a three-layer slab model of Pt(111) as...
benchmark (for details see Supporting Information). Under neutral pH conditions, ORR generally involves four intermediate species, i.e. surface-adsorbed $\text{O}_2^*$, $\text{OOH}^*$, $\text{O}^*$, and $\text{OH}^*$. Thus, moderate free energies of adsorption for these intermediates are crucial in determining the catalytic efficiency. Figure 5b illustrates the Gibbs free energy diagrams for ORR by $\text{Fe}_7$ and the Pt(111) surface calculated based on the theoretical framework developed by Nørskov et al.\[5\] Our initial data suggest that $\text{O}_2$ adsorption on $\text{Fe}_7$ is 0.37 eV more favorable than on the classical Pt(111), suggesting that iron oxo clusters might be acting as active oxygen transporters for ORR reactions. The following ORR reaction steps proceed energetically downhill, and desorption of $\text{OH}^*$ is determined as the rate-limiting step. This initial theoretical analysis suggests that future experimental studies on the use iron oxide clusters as ORR catalysts are warranted and could lead to new, noble metal-free molecular ORR catalysts.

In sum, we present the first example of the use of molecular iron oxide clusters as soluble enhancers for electrocatalytic reactions. Solutions containing the high-nuclearity $\text{Fe}_{28}$ iron oxide cluster show synergistic enhancement of the oxygen reduction reaction when operated with standard Pt/C catalysts in aqueous solution at near-neutral pH. Initial mechanistic studies suggest that the $\text{Fe}_{28}$ solutions allow improved $\text{O}_2$ mass transport from the gas phase to the liquid phase and on to the solid Pt/C catalyst. Comparative studies with a FeCo alloy ORR catalyst show that this catalytic performance improvement of $\text{Fe}_{28}$ can be generalized to other ORR catalyst classes. The results obtained from principal electrochemical studies were transferred to the device level and showed significantly improved performance when operated in a direct formate microfluidic fuel cell. Future work will study the role of $\text{Fe}_{28}$ under operating conditions to gain further experimental and theoretical insights into the mechanism of reactivity enhancement.

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