

Contract No.:

This manuscript has been authored by Battelle Savannah River Alliance (BSRA), LLC under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes.

On the lack of correlation between the voltammetric redox couple and ORR activity of Fe-N-C catalysts

Authors

| | |
|----------------------------------------|-----------------------------------|
| Mark C. Elvington ¹ | mark.elvington@srnl.doe.gov |
| Hoon T. Chung ² | hchung@lanl.gov |
| Ling Lin ² | linglin@lanl.gov |
| Xi Yin ² | xiyin@lanl.gov |
| Prabhu Ganesan ¹ | prabhu.ganesan@srnl.doe.gov |
| Piotr Zelenay ^{z,2} | zelenay@lanl.gov |
| Héctor R. Colón-Mercado ^{z,1} | hector.colon-mercado@srnl.doe.gov |

Affiliations

- ¹ Energy Materials
Savannah River National Laboratory
Aiken, South Carolina, 29808, USA
- ² Materials Physics and Applications Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545, USA

^z Corresponding authors

Abstract

Platinum group metal-free catalysts for polymer electrolyte fuel cells are analyzed in different electrolytes (H_2SO_4 and HClO_4) and at different pH's to gain insight into the oxygen reduction reaction (ORR) mechanism. Two Fe-N-C type catalysts each show a reversible voltammetric redox couple around 0.77 V vs. RHE in HClO_4 electrolyte. A notable cathodic shift of the redox couple to 0.62 V is observed in H_2SO_4 and is assigned to bisulfate adsorption. Concurrently, the ORR activity of the catalysts is unaffected, suggesting an independent nature of the reductive mechanism with the redox peak species.

Keywords

Fuel cells, oxygen reduction reaction, PGM-free catalysts, reversible redox couple, pH dependence

1 Introduction

Transition metal-nitrogen-carbon (M-N-C) platinum group metal-free (PGM-free) catalysts are an emerging alternative to Pt-based catalysts for polymer electrolyte fuel cells (PEFCs).¹⁻⁵ Early PGM-free catalysts were heme-inspired pyrolyzed MN₄ macrocycles, consisting of pyrrolic- or pyridinic-N heterocycles, coordinated to Fe or Co^{6,7} promoting either a 4e⁻ or 2×2e⁻ reduction of oxygen.^{8,9} Recently, significant improvements to the ORR activity for Fe-N-C type catalysts in acidic media have been achieved,¹⁰ however, the ORR activity is still inferior to that of the Pt-based catalysts.¹¹ To improve the activity of PGM-free catalysts a comprehensive understanding of the nature of ORR active site(s) is required. The origins of the ORR activity of M-N-C catalysts have been debated for several decades, however, their nature remains indeterminate.^{12,13} While the presumed requirement of a coordinated transition metal and its role in the ORR has recently come into question,¹⁴⁻¹⁶ much of the available data supports the hypothesis that the presence of a coordinated metal is critical to achieving high ORR activity.^{1,17,18}

Among several approaches used in studying the ORR active sites in Fe-N-C catalysts, efforts to correlate the potential of redox peak in Fe-N-C catalysts to ORR activity have been reported. Depending on the type of PGM-free catalyst, redox-active species such as quinone/hydroquinone groups can be observed such as in oxidized carbonaceous materials.¹⁹ However, the quinone/hydroquinone redox-couple does not seem to correlate with the ORR activity of the PGM-free catalysts in acidic medium.^{20,21} Typically, voltammograms of Fe-containing catalysts reveal the presence of a reversible redox-couple in the potential range between 0.64 and 0.78 V vs. RHE,^{9,22-25} often attributed to the Fe³⁺/Fe²⁺ couple.^{9,24,25} It has been proposed that Fe must be in the 2+ oxidation state to be active for ORR. For example, Jia *et al.* suggested that at potentials higher than the Fe³⁺/Fe²⁺ redox potential, Fe in the valence state of 3+ is poisoned

by oxygen species and thus not available for adsorption of O₂.⁵ Zagal *et al.* also claimed that Fe³⁺ cannot be an active site as this site is poisoned by OH.²⁶ Similarly, Kramm *et al.* precluded Fe³⁺ from being an active site based on the same notion that O₂ can only adsorb on Fe²⁺ sites,²⁷ a view supported by Osmieri *et al.*²⁸ Thus, according to these studies, Fe-N-C catalysts are active only at potentials lower than the Fe³⁺/Fe²⁺ redox potential, *i.e.*, in the 2+ oxidation state of Fe. In this work, two Fe-N-C catalysts were studied via electrochemical methods in two acid electrolytes under varying conditions, with the purpose of elucidating any link, or lack thereof, between the reversible redox couple and the ORR activity.

2 Experimental

2.1 Catalyst synthesis and characterization

Refer to supplementary information.

2.2 Electrochemical measurements

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and potential-step chronoamperometry (PSC) were performed to characterize the ZIF-8 and (CM+PANI)-Fe-C(Zn) catalysts using a WaveDriver® 20 bi-potentiostat, a 5.5 mm diameter glassy-carbon rotating disc electrode (RDE; Pine Instrument Company), and a graphite rod counter electrode in N₂- or O₂-saturated 0.5 M H₂SO₄ or HClO₄ electrolyte (unless specified otherwise) at room temperature. A Pt wire submerged in H₂-saturated 0.5 M H₂SO₄ (reversible hydrogen electrode; RHE) or 1.0 M HClO₄ (normal hydrogen electrode; NHE) was used as a reference electrode. CV measurements were recorded at 20 mV/s. Redox potentials were determined by measuring the anodic and cathodic peaks and calculating the half-way point. For ZIF-8-derived catalysts, LSV scans were performed at 5 mV/s in N₂-saturated electrolyte to measure background current, and with O₂ for ORR measurements at 900 rpm. For (CM+PANI)-Fe-C(Zn) catalysts, steady-state PSC plots were

recorded in O₂-saturated electrolyte using a 20 mV/20 s steps at 900 rpm.

3 Results and discussion

3.1 Electrochemical characterization of ZIF-8-derived catalysts

The CV and RDE test data reveal a different electrochemical behavior depending on the Fe content within the series of ZIF-8-derived catalysts. The CV shows a well-defined redox couple at approximately 0.66 V vs. RHE in 0.5 M H₂SO₄ (**Figure 1**), which is sometimes seen in other PGM-free Fe-N-C type catalysts.^{9,24,25} The origin of this redox couple has not been definitively identified. Both the Fe³⁺/Fe²⁺ couple^{9,24,25} and quinone/hydroquinone-type^{29,30} couples have been suggested to be responsible for this redox feature, with no conclusive evidence presented to date. In the present work, the redox couple at *ca.* 0.66 V for the ZIF-8 derived catalysts (**Figure 1**) increases in magnitude with increasing iron content, alluding to a possible Fe-based nature. **Figure 1b** shows the ORR performance of ZIF-8-derived catalyst measured in 0.5 M H₂SO₄.

The redox-couple potential shows a strong dependency on the type of the electrolyte used in electrochemical testing. In one experiment, the total molar concentration of the acid electrolytes, HClO₄ and H₂SO₄, *i.e.*, the solution pH, was kept constant at 0.5 M, while the ratio of HClO₄ and H₂SO₄ was varied. The redox couple potential was found to increase gradually with increasing HClO₄ content (**Figure 2a**), from *ca.* 0.66 V in 0.5 M H₂SO₄ to 0.77 V in 0.5 M HClO₄. LSV scans were measured in O₂-saturated HClO₄ and H₂SO₄, to determine if there is a connection between the electrolyte, redox-couple potential, and ORR current. Despite the differences in the redox couple potential in N₂-saturated solutions (**Figure 2a**), the ORR activity of the catalyst was essentially the same in the two acids (**Figure 2b**). The ORR onset potential of 0.95 V was identical in HClO₄ and H₂SO₄, as was the response in the kinetic range of ORR potentials (up to *ca.* 0.8 V).

Only the limiting current values were found to be different in the two acids, likely due to differences in the oxygen diffusivity and solubility.³¹

3.2 Electrochemical characterization of (CM+PANI)-Fe-C(Zn) catalyst

Also studied in 0.5 M HClO₄ and 0.5 M H₂SO₄ electrolytes was an Fe-based catalyst derived from (CM+PANI)-Fe-C(Zn). The results were similar to those obtained with the ZIF-8 catalysts. Redox-couple potentials of 0.61 V and 0.77 V were measured in 0.5 M H₂SO₄ and 0.5 HClO₄, respectively. The redox potential again was found to increase with increasing HClO₄ content (**Figure 3a**). No difference in the ORR activity was observed between the two electrolytes, with the onset potential and catalyst behavior in the kinetic region being identical in both cases (**Figure 3b**). As before, no correlation between the redox couple potential and ORR activity was found for the (CM+PANI)-Fe-C(Zn) catalyst. The data in **Figures 2** and **3** indicates that the species responsible for the reversible redox couple observed in the voltammograms recorded for these two electrocatalysts, and likely for other Fe-N-C ORR electrocatalysts, plays no role in the oxygen reduction reaction.

3.3 Quinone/hydroquinone-type and Fe³⁺/Fe²⁺ redox couples

Both the Fe³⁺/Fe²⁺ and the quinone/hydroquinone-type redox couples have been suggested to be responsible for the voltammetric redox feature observed in Fe-N-C type catalysts. An additional experiment was conducted to elucidate the redox-couple origin. The standard potentials for Fe³⁺/Fe²⁺ and quinone/hydroquinone redox reactions are:³²



In the present work, the redox-couple potential measured for ZIF-8-derived and (CM+PANI)-Fe-C(Zn) catalysts was 0.77 V vs. RHE in 0.5 M HClO₄, or 0.75 V vs. SHE (E_{RHE} =

$E_{\text{SHE}} + 0.059 \times \text{pH}$, where $E_{\text{SHE}} = 0 \text{ V}$). The proximity of the observed redox potential to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple,³² suggests that the species responsible could be Fe-based. A quinone/hydroquinone based redox couple should be pH-dependent, with an expected potential shift of $-59.2 \text{ mV}/(\text{pH unit})$ (eq2). Experimentally, a pH dependence of $-57.3 \text{ mV}/(\text{pH unit})$ has been measured for quinone/hydroquinone,²⁹ and values of -50 to $-60 \text{ mV}/(\text{pH unit})$ for substituted quinones.^{29,30} In this work, CVs were recorded with $\text{HClO}_4/\text{LiClO}_4$ electrolyte to produce a range of pH values while maintaining constant ClO_4^- concentration. As shown in **Figure 4**, the change in the solution pH from 0.67 to 1.21 resulted in a small shift in the redox couple potential, -4 mV and $+8 \text{ mV}$ for the ZIF-8 and CM+PANI derived catalysts, respectively. This observed shift is smaller than the expected 32 mV shift for a quinone species suggesting that the observed voltammetric behavior is due to a non-quinone species.

3.4 Impact of electrolyte and adsorbed species on the redox potential and the ORR

An important matter to consider is the observed difference in the redox potentials measured in H_2SO_4 and HClO_4 . The measured redox-couple potentials were 0.77 V in 0.5 M HClO_4 and $0.61\text{-}0.66 \text{ V}$ in $0.5 \text{ M H}_2\text{SO}_4$, alluding to a possible effect by H_2SO_4 . Sulfate and bisulfate adsorption has been well documented in Pt electrocatalysis,³³ but never reported for PGM-free catalysts. If adsorption of the anions (bisulfate at the pH used for the analysis) can occur on PGM-free catalysts, based on electrochemical data alone it is difficult to discern the type of site(s) that bisulfate has the highest affinity to (*e.g.*, iron, iron carbides, Fe-N-C moieties, or pyridinic nitrogen). Following extensive purification one can exclude the presence of Fe^0 and iron carbide particles. However, those tend to be fully encapsulated and isolated by graphitic carbon species.³⁴ While the nature of the sites binding the anions is unclear, the ORR data in **Figures 2 and 3** leaves no doubt that adsorption of ions occurs on sites not involved in the ORR.

Compounds that are likely to act as active-site poisons have been employed in recent studies on PGM-free catalysts to study their effect on the ORR.^{9,35} Tylus *et al.*⁹ used cyanide (CN^-) in acidic and alkaline media and found that CN^- can inhibit the ORR, which shifted towards higher overpotential values. Additionally, CN^- slightly suppressed the redox peak current and shifted its potential negatively. This behavior was attributed to the inhibition of the Fe-N centers through the formation of a strong cyanide coordination bond with Fe^{3+} .³⁶ In this work, a significant negative shift in the redox-couple potential by 0.11 V was observed with ZIF-8-derived and (CM+PANI)-Fe-C catalysts after replacing HClO_4 with H_2SO_4 . However, since no change in the ORR activity was measured, the bisulfate adsorption does not appear to affect the active site(s). Recently, Li *et al.*²⁴ investigated the site-blocking effect arising from $\text{Fe}^{3+}\text{-OH}_{\text{ads}}$ and its role in limiting the ORR. The authors suggested that the active site blocking effect could be used as an activity descriptor. It was concluded that the ORR activity was inversely dependent on the OH_{ads} surface coverage, whereby an increase in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox-couple potential resulted in an increase in the fraction of unoccupied sites and, consequently, in improved catalytic activity. In contrast, DFT calculations point to possible enhancement in the ORR activity of FeN_x sites in PGM-free catalysts once coordinated by an OH ligand from spontaneous decomposition of water.³⁷ The results reported in this work for two active PGM-free catalysts do not follow the aforementioned trends, with no correlation observed between the ORR activity and the redox-couple potential.

According to the hypothesis that the FeN_x moieties involving pyridinic and/or pyrrolic nitrogen are the active sites,^{10,12,13,38-40} the adsorption of bisulfate on the surface could have an impact on the ORR. Adsorption of the electron-rich bisulfate at or near the pyridinic/pyrrolic nitrogen atoms can result in increased availability of the nitrogen lone electron pairs, increased basicity,^{41,42} and enhanced σ donation to the Fe atoms in FeN_x moieties. An increase in the electron

density at the Fe atom would lead to a negative shift in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential.⁴³ Such a shift is observed in the voltammograms and can involve Fe-containing moieties, but other species can also behave similarly. The reversible potential of any redox-active surface species near the adsorbed bisulfate can be affected the same way. Since no change in the ORR activity was measured for the ZIF-8-derived and (CM+PANI)-Fe-C(Zn) catalysts, the observed redox-couple is unlikely to be the ORR active site in these two catalysts or, for that matter, alter the electronic state of the active site. However, there is still a possibility of a direct link between the redox potential and the ORR if the bisulfate ion is displaced by the dissolved oxygen in the electrolyte during the ORR. Further studies are needed to understand a possible indirect role of the surface redox couple in the ORR on Fe-based PGM-free catalysts.

4 *Summary*

The electrochemical behavior of ZIF-8-derived and (CM+PANI)-Fe-C(Zn) ORR catalysts was studied. A reversible redox couple was identified in the voltammetry recorded for both catalysts. The redox-couple potential was determined to be 0.77 V in 0.5 M HClO_4 and between 0.62 and 0.66 V in 0.5 M H_2SO_4 signifying a strong correlation between the redox couple potential and bisulfate adsorption. No correlation between the redox potential and the ORR activity was observed for the ZIF-8-derived and (CM+PANI)-Fe-C(Zn) catalysts. Based on its behavior in solutions with different pH, it is concluded that the observed voltammetry does not arise from the reduction/oxidation of quinone/hydroquinone-type species. These electrochemical observations call for the re-examination of ORR mechanistic studies in PGM-free catalysts.

Acknowledgements

The Savannah River National Laboratory effort was supported by the LDRD program. Savannah River National Laboratory is managed and operated by Savannah River Nuclear Solutions, LLC

under Contract No. DE-AC09-08SR22470 with the United States Government. Los Alamos National Laboratory effort was supported by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy, Hydrogen and Fuel Cell Technologies Office, through the Electrocatalysis Consortium.

References

1. M. Lefevre, E. Proietti, F. Jaouen, J.P. Dodelet, *Science* 324 (2009) 71-74.
2. G. Wu, K.L. More, C.M. Johnston, P. Zelenay, *Science* 332 (2011) 443-447.
3. E. Proietti, F. Jaouen, M. Lefevre, N. Larouche, J. Tian, J. Herranz, J.P. Dodelet, *Nature Communications* 2 (2011).
4. J.L. Shui, C. Chen, L. Grabstanowicz, D. Zhao, D.J. Liu, *Proceedings of the National Academy of Sciences of the United States of America* 112 (2015) 10629-10634.
5. J.K. Li, S. Ghoshal, W.T. Liang, M.T. Sougrati, F. Jaouen, B. Halevi, S. McKinney, G. McCool, C.R. Ma, X.X. Yuan, Z.F. Ma, S. Mukerjee, Q.Y. Jia, *Energ Environ Sci* 9 (2016) 2418-2432.
6. J.A.R. Vanveen, H.A. Colijn, J.F. Vanbaar, *Electrochimica Acta* 33 (1988) 801-804.
7. J.Y. Cheon, T. Kim, Y. Choi, H.Y. Jeong, M.G. Kim, Y.J. Sa, J. Kim, Z. Lee, T.H. Yang, K. Kwon, O. Terasaki, G.G. Park, R.R. Adzic, S.H. Joo, *Scientific Reports* 3 (2013).
8. T.S. Olson, S. Pylypenko, J.E. Fulghum, P. Atanassov, *J. Electrochem. Soc.* 157 (2010) B54-B63.
9. U. Tylus, Q.Y. Jia, K. Strickland, N. Ramaswamy, A. Serov, P. Atanassov, S. Mukerjee, *Journal of Physical Chemistry C* 118 (2014) 8999-9008.
10. K. Artyushkova, A. Serov, S. Rojas-Carbonell, P. Atanassov, *Journal of Physical Chemistry C* 119 (2015) 25917-25928.
11. H.G. Zhang, H. Osgood, X.H. Xie, Y.Y. Shao, G. Wu, *Nano Energy* 31 (2017) 331-350.
12. A. Zitolo, V. Goellner, V. Armel, M.T. Sougrati, T. Mineva, L. Stievano, E. Fonda, F. Jaouen, *Nature Materials* 14 (2015) 937-945.
13. N.R. Sahraie, U.I. Kramm, J. Steinberg, Y.J. Zhang, A. Thomas, T. Reier, J.P. Paraknowitsch, P. Strasser, *Nature Communications* 6 (2015).
14. S. Maldonado, K.J. Stevenson, *Journal of Physical Chemistry B* 109 (2005) 4707-4716.
15. X.G. Li, G. Liu, B.N. Popov, *Journal of Power Sources* 195 (2010) 6373-6378.
16. P.H. Matter, E. Wang, J.M.M. Millet, U.S. Ozkan, *Journal of Physical Chemistry C* 111 (2007) 1444-1450.
17. F. Jaouen, S. Marcotte, J.P. Dodelet, G. Lindbergh, *Journal of Physical Chemistry B* 107 (2003) 1376-1386.
18. H. Schulenburg, S. Stankov, V. Schunemann, J. Radnik, I. Dorbandt, S. Fiechter, P. Bogdanoff, H. Tributsch, *Journal of Physical Chemistry B* 107 (2003) 9034-9041.
19. J. Maruyama, I. Abe, *Electrochimica Acta* 46 (2001) 3381-3386.
20. N. Alexeyeva, K. Tammeveski, *Electrochemical and Solid State Letters* 10 (2007) F18-F21.
21. I. Kruusenberg, N. Alexeyeva, K. Tammeveski, J. Kozlova, L. Matisen, V. Sammelselg, J. Solla-Gullon, J.M. Feliu, *Carbon* 49 (2011) 4031-4039.

22. X.L. Wang, Q. Li, H.Y. Pan, Y. Lin, Y.J. Ke, H.Y. Sheng, M.T. Swihart, G. Wu, *Nanoscale* 7 (2015) 20290-20298.
23. X.J. Wang, H.G. Zhang, H.H. Lin, S. Gupta, C. Wang, Z.X. Tao, H. Fu, T. Wang, J. Zheng, G. Wu, X.G. Li, *Nano Energy* 25 (2016) 110-119.
24. J.K. Li, A. Alsudairi, Z.F. Ma, S. Mukerjee, Q.Y. Jia, *Journal of the American Chemical Society* 139 (2017) 1384-1387.
25. J. Chlistunoff, *The Journal of Physical Chemistry C* 115 (2011) 6496-6507.
26. J.H. Zagal, M.T.M. Koper, *Angew Chem Int Edit* 55 (2016) 14510-14521.
27. U.I. Kramm, M. Lefevre, N. Larouche, D. Schmeisser, J.P. Dodelet, *J Am Chem Soc* 136 (2014) 978-985.
28. L. Osmieri, R.K. Ahluwalia, X.H. Wang, H.T. Chung, X. Yin, A.J. Kropf, A.E.Y. Park, D.A. Cullen, K.L. More, P. Zelenay, D.J. Myers, K.C. Neyerlin, *Appl Catal B-Environ* 257 (2019).
29. M.M. Walczak, D.A. Dryer, D.D. Jacobson, M.G. Foss, N.T. Flynn, *Journal of Chemical Education* 74 (1997) 1195-1197.
30. G. Jurmann, D.J. Schiffrin, K. Tammeveski, *Electrochimica Acta* 53 (2007) 390-399.
31. K.E. Gubbins, R.D. Walker, *J. Electrochem. Soc.* 112 (1965) 469-471.
32. *CRC Handbook of Chemistry and Physics*, CRC press, 2014.
33. N. Markovic, H. Gasteiger, P.N. Ross, *J. Electrochem. Soc.* 144 (1997) 1591-1597.
34. X.-H. Yan, P. Prabhu, H. Xu, Z. Meng, T. Xue, J.-M. Lee, *Small Methods* 4 (2020) 1900575.
35. D. Malko, A. Kucernak, T. Lopes, *Nature Communications* 7 (2016).
36. Q.Y. Jia, N. Ramaswamy, U. Tylus, K. Strickland, J.K. Li, A. Serov, K. Artyushkova, P. Atanassov, J. Anibal, C. Gumeci, S.C. Barton, M.T. Sougrati, F. Jaouen, B. Halevi, S. Mukerjee, *Nano Energy* 29 (2016) 65-82.
37. H.T. Chung, D.A. Cullen, D. Higgins, B.T. Sneed, E.F. Holby, K.L. More, P. Zelenay, *Science* 357 (2017) 479-483.
38. M. Lefevre, J.P. Dodelet, P. Bertrand, *Journal of Physical Chemistry B* 106 (2002) 8705-8713.
39. M. Ferrandon, X.P. Wang, A.J. Kropf, D.J. Myers, G. Wu, C.M. Johnston, P. Zelenay, *Electrochimica Acta* 110 (2013) 282-291.
40. H.T. Chung, C.M. Johnston, K. Artyushkova, M. Ferrandon, D.J. Myers, P. Zelenay, *Electrochem. Commun.* 12 (2010) 1792-1795.
41. G.L. Miessler, D.A. Tarr, *Inorganic chemistry*, 2nd ed., Upper Saddle River, N.J. : Prentice Hall, 1999.
42. H.C. Brown, *Journal of the Chemical Society* (1956) 1248-1268.
43. S.C. Rasmussen, M.M. Richter, E. Yi, H. Place, K.J. Brewer, *Inorganic Chemistry* 29 (1990) 3926-3932.

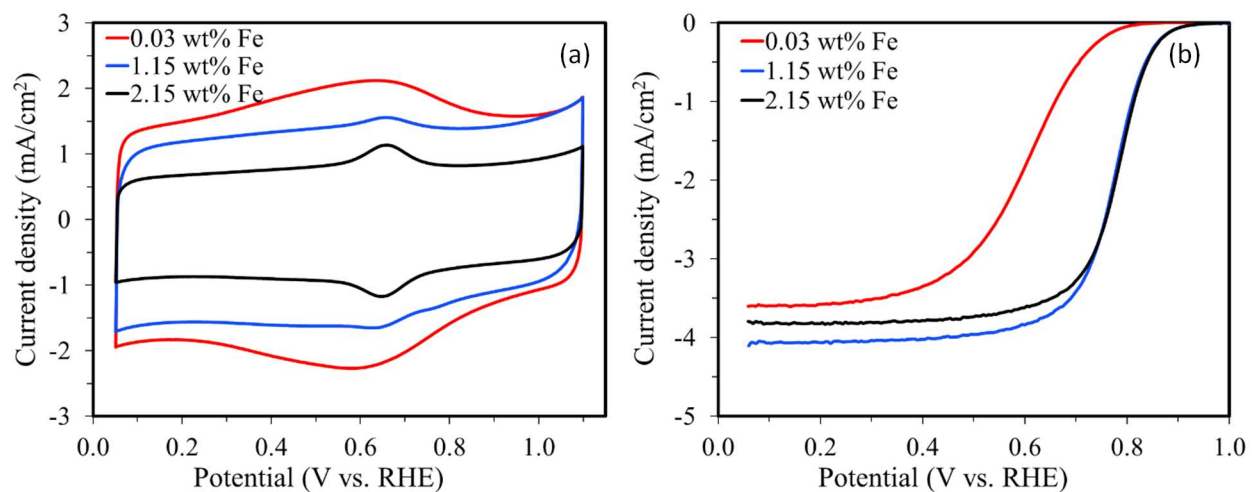


Figure 1. (a) Cyclic voltammetry of ZIF-8-derived catalysts in N₂-saturated 0.5 M H₂SO₄ showing the effect of Fe content on the redox couple. **(b)** ORR polarization plots; 0.5 M H₂SO₄.

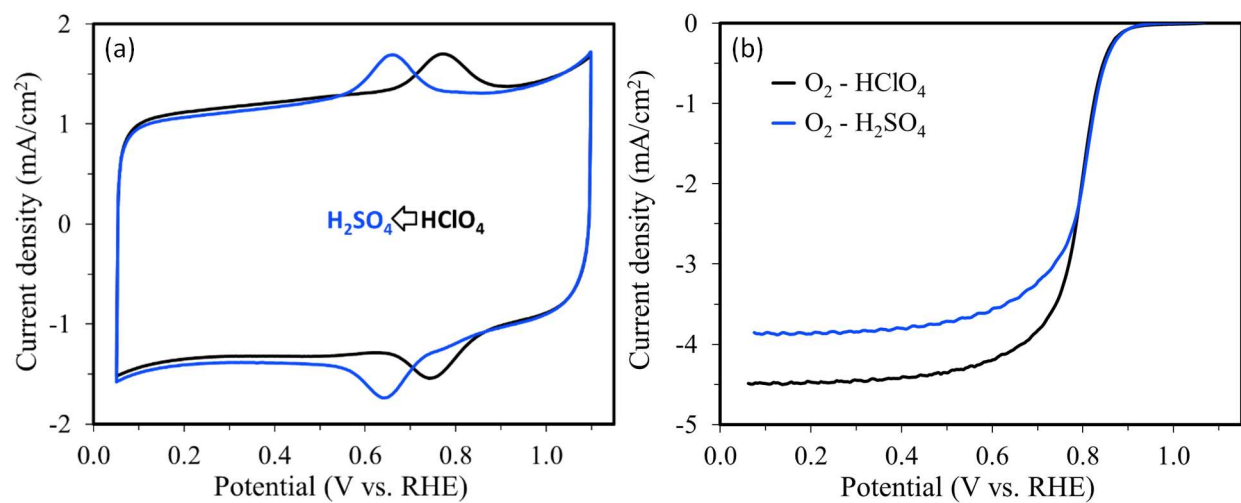


Figure 2. (a) Cyclic voltammetry of ZIF-8-derived catalyst (2.15 wt% Fe) in N_2 -saturated solution showing effect of electrolyte composition on the redox-couple potential. (b) LSV plots in O_2 -saturated 0.5 M HClO_4 and 0.5 M H_2SO_4 .

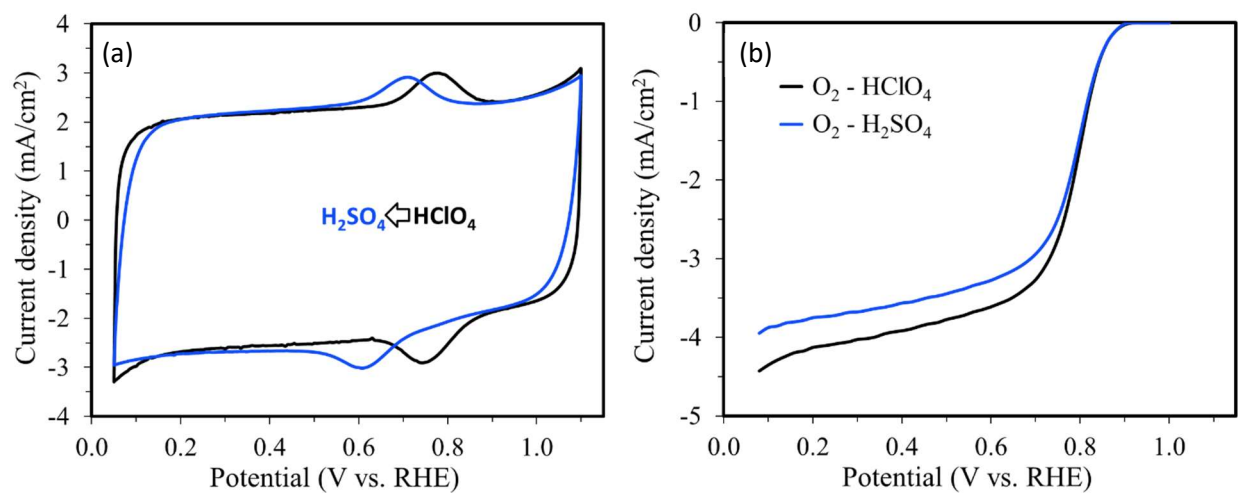


Figure 3. (a) Cyclic voltammetry of (CM+PANI)-Fe-C(Zn) catalyst in N₂-saturated solution showing the effect of electrolyte composition on the redox-couple potential. (b) PSC plots in O₂-saturated 0.5 M HClO₄ and 0.5 M H₂SO₄.

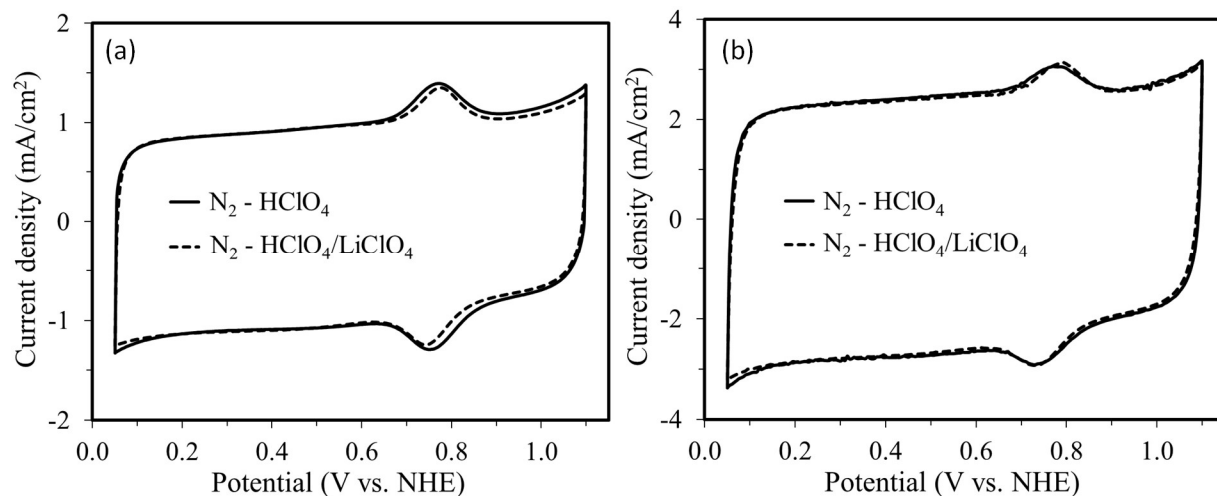


Figure 4. (a) Cyclic voltammetry of ZIF-8-derived (2.15 wt% Fe) catalyst in N₂-saturated solution showing effect of pH on redox-couple potential. (b) Cyclic voltammetry of (CM+PANI)-Fe-C(Zn) in N₂-saturated solution showing effect of pH on redox couple potential.