Results in Chemistry 28 (2026) 103563

Contents lists available at ScienceDirect

Results in Chemistry

journal homepage: www.sciencedirect.com/journal/results-in-chemistry

Proton availability governs the high-current oxygen reduction reaction in a gas diffusion electrode

Aleš Marsel [a,b,*], Miha Hotko [a,c], Nik Maselj [a], Nejc Hodnik [a,c]

[a] National Institute of Chemistry, SI-1000 Ljubljana, Slovenia
[b] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana SI-1000, Slovenia
[c] University of Nova Gorica, Nova Gorica SI-5000, Slovenia

ARTICLE INFO

Keywords:
Oxygen reduction reaction
Gas diffusion electrode
Proton transport
High current density
Electrolyte concentration
PEM fuel cells

ABSTRACT

Gas diffusion electrodes enable oxygen reduction reaction studies at current densities beyond the limits of rotating disk electrodes, yet the role of electrolyte proton availability remains unclear. Herein, oxygen reduction polarization curve behavior was investigated using 0.1–2 M $HClO_4$. While cyclic voltammetry and electrochemical surface area were consistent, current plateaus emerged at low acid concentrations. These results show that proton transport can limit the achievable current density. Achieving current densities of 1 A cm^{-2} required at least 0.8 M $HClO_4$, while 2 M $HClO_4$ was necessary to reach 2 A cm^{-2}. These findings provide practical guidance for electrolyte selection in high-current gas diffusion electrode measurements and demonstrate that they can serve as a platform for studying proton transport behavior.

Introduction

The global push for sustainable energy has placed proton exchange membrane fuel cells (PEMFC) back at the forefront of electrochemical research. A major part of this effort involves optimizing oxygen reduction reaction (ORR), which remains the primary source of voltage loss in these devices. To study this reaction under industrially relevant conditions, the field has increasingly moved toward systems like the gas diffusion electrode (GDE). Such setups are essential because they allow for current densities well above 1 A cm^{-2}, far exceeding the mass transport limited current densities of a traditional rotating disk electrode (RDE) [1,2].

The choice of electrolyte concentration used in literature has become a point of some variation. In RDE experiments, 0.1 M $HClO_4$ is commonly used because it provides a relatively weakly adsorbing benchmark electrolyte environment for kinetic studies [3,4]. Nevertheless, electrolyte composition and proton-conducting environment are known to influence ORR kinetics through changes in ionic conductivity, proton mobility, and specific anion interactions with Pt surfaces [5–7]. However, in GDEs, researchers typically utilize much higher concentrations, such as 1 M or 2 M $HClO_4$, to reduce ohmic resistance and better simulate the pH environment of a polymer membrane. In some cases, concentrations as high as 5 M have been tested to explore the limits of catalyst loading and proton availability [8,9]. Alternative proton-conducting environments, including concentrated phosphoric acid systems, have also been investigated in GDE studies under fuel-cell-relevant conditions [10]. In others, due to the limitations of other instrumentation, the concentration was limited to only 0.1 M [11,12].

Despite the frequent use of different electrolytes, there is a lack of data on how the transition from low to high concentrations of $HClO_4$ actually changes the behavior of the GDE. Although electrolyte effects on ORR kinetics have been widely studied at the RDE level, systematic investigations of proton transport limitations under high-current-density GDE operation remain scarce. While it is generally understood that acid concentration affects parameters such as ionic conductivity, a systematic analysis of how this transition is reflected in ORR polarization curves at industrially relevant current densities is still lacking. We note that, at the RDE level, perchlorate has been reported to specifically adsorb on Pt(1 1 1), slightly inhibiting ORR kinetics at potentials above approximately 0.8 V [13]. In addition, scan rate can also affect the measured ORR response [14]. In this communication, we directly compare ORR performance in a GDE setup across the 0.1–2 M $HClO_4$ range, focusing on high-current-density behavior below 0.8 V. The results show that proton transport, rather than oxygen transport, limits the maximum achievable current density. More broadly, they demonstrate that GDE setups can serve not only for catalyst screening, but also as a

* Corresponding author at: National Institute of Chemistry, SI-1000 Ljubljana, Slovenia.
E-mail address: ales.marsel@ki.si (A. Marsel).

https://doi.org/10.1016/j.rechem.2026.103563
Received 5 May 2026; Accepted 14 June 2026
Available online 17 June 2026

platform for probing proton transport limitations under membrane-relevant conditions.

Experimental

Suspension was prepared using catalyst powder (50% Pt/C Johnson Matthey), a solvent of 1:1 ratio of water and isopropanol, and with a 0.7 I/C ratio of Nafion® (5 wt% D520 Nafion® solution, Ion Power). The prepared suspension was ultrasonicated with an ultrasonic horn (Branson) for 15 min of total sonication time (2 s on, 1 s off). The suspension was spraycoated onto a gas diffusion layer with a microporous layer (Sigracet® 39BB, FuelCellStore) with an ultrasonic spray nozzle (Siansonic). The surface area was limited to a 3 mm diameter circle (0.0707 cm^2) using a mask. The total geometric Pt loading was determined using X-ray fluorescence (ThermoScientific ARL™ QuantX EDXRF Analyzer) to be 109 ± 3 $\mu g_{Pt}/cm^2$.

Electrochemical measurements were performed with a CS310X (CorrTest) potentiostat with an in-house developed cell, similar to the ones in literature [2,9]. The counter electrode was a mixed-metal oxide mesh (Metakem). A $Hg/HgSO_4$ (CorrTest) reference electrode was used. All the potentials mentioned in this work are given vs RHE. Measurements were performed in 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 M $HClO_4$ (Supra qualität, ROTH) at room temperature.

Initially, the samples were cycled 50 times from 0.05 to 1.2 V at 200 mV/s to clean the surface of the catalyst. For the determination of electrochemical surface area (ECSA) 3 cycles were performed at 50 and 100 mV/for each sample. The uncompensated resistance was determined by high-frequency resistance measurement at 10 kHz at 0.1 V vs RHE. During electrochemical measurements, 85% iR compensation was applied in situ, while the remaining 15% was corrected post-measurement. 85% iR drop compensation was applied during the measurement, with the additional 15% compensated post-mortem. To ensure repeatability, three samples were measured for each concentration of acid. All samples showed very good reproducibility with a relative error of less than 10%. Gas flow was kept constant at 50 mL min^{-1} to minimize changes in oxygen mass transport and ensure that the observed performance shifts primarily reflected the electrolyte environment. The gases were humidified using a bubbler before reaching the measurement cells.

Results and discussion

In a conventional RDE setup, the current is rapidly limited to approximately 6 mA cm^{-2} at 1600 rpm by the mass transport of dissolved oxygen to the catalyst surface. This limitation arises from the low solubility of oxygen in aqueous electrolytes, which is only in the ppm range. In contrast, GDE setups overcome this restriction by supplying oxygen directly in the gas phase, thereby enabling current densities above 1 A cm^{-2}. Under these conditions, proton availability in the liquid electrolyte can become rate-limiting. At low acid concentration, such as 0.1 M $HClO_4$, a clear current-density limit is observed, indicating insufficient proton transport to sustain higher ORR rates. In Fig. 1, we show that the voltammogram does not change significantly when the concentration of acid is between 0.1 M and 2 M $HClO_4$ [14]. This is also supported in Fig. 2, where we can see that the ECSA does not change significantly, and the ECSA of all acid concentrations are in the range of errors of the triplicates. In contrast, Fig. 3 reveals a strong dependence of ORR performance on acid concentration, with clear plateaus appearing at lower $HClO_4$ concentrations. This decoupling between ECSA and ORR activity indicates that proton availability is sufficient for hydrogen underpotential deposition (Hupd) and surface area determination but becomes limiting during ORR operation at high current densities. Unlike ECSA measurements, which involve relatively small proton fluxes near equilibrium conditions, the ORR consumes protons continuously and at much higher rates. Consequently, proton transport limitations only become apparent under ORR conditions, where the local proton demand

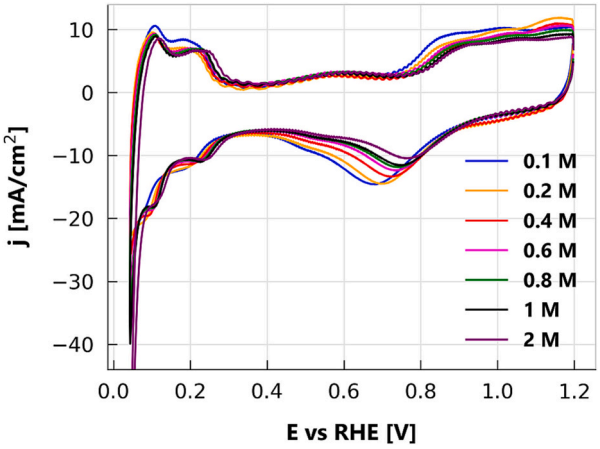

Fig. 1. Cyclic voltammograms of Pt/C GDEs recorded in different $HClO_4$ concentrations at room temperature. The scan rate was 200 mV/s, the geometric Pt loading was 109 ± 3 μg_{Pt} cm^{-2}_{geo}, and 85% iR compensation was applied during measurement with the remaining 15% corrected post-measurement.

exceeds the transport capability of dilute electrolytes.

This behavior is consistent with previous studies on proton-coupled electrochemical reactions, where local proton depletion near the electrode surface has been shown to significantly alter reaction kinetics and local pH under high reaction-rate conditions. Similar effects have been reported for the HOR/HER on Pt electrodes, where proton consumption or generation leads to substantial near-surface concentration gradients even when the bulk electrolyte composition remains unchanged [15]. The present results suggest that an analogous local proton depletion mechanism occurs during high-current-density ORR in GDE systems, resulting in the observed transport-limited current plateaus at low $HClO_4$ concentrations.

Since most GDE studies aim to access high-current-density ORR operation, the results in Fig. 3 show that $HClO_4$ concentrations below 0.8 M lead to apparent proton-transport limitations before reaching 1 A cm^{-2} under the present experimental conditions. Measurements targeting 2 A cm^{-2} require 2 M $HClO_4$ to avoid such limitations.

Although the present results clearly demonstrate proton transport limitations in GDE measurements, several factors related to catalyst-layer composition and transport mechanisms should be considered when generalizing these findings. It should be noted that the present study was conducted using a single commercial 50 wt% Pt/C catalyst, and therefore the quantitative proton transport limitations observed here may depend on the specific catalyst-layer architecture. Parameters such as Pt loading, ionomer content, catalyst-layer thickness, and Pt particle size can influence the local proton transport resistance and water distribution within the catalyst layer, thereby affecting the onset and severity of proton transport limitations.

Nevertheless, the observed current plateaus at low acid concentrations are expected to be a more general characteristic of high-current-density GDE measurements, since the ORR intrinsically requires significant proton flux to sustain large reaction rates. While the exact limiting current densities may vary between catalyst systems, the overall trend of increasing proton transport limitations with decreasing electrolyte acidity should remain broadly applicable.

The proton transport limitation observed in this work likely arises from a combination of proton diffusion and migration effects within the electrolyte and catalyst layer. At high current densities, rapid proton consumption near the catalyst surface can generate local proton concentration gradients, particularly at lower $HClO_4$ concentrations, where the available proton concentration and electrolyte conductivity are reduced. Under these conditions, proton diffusion alone may become insufficient to replenish consumed protons at the required rate, while the reduced ionic conductivity also limits proton migration through the

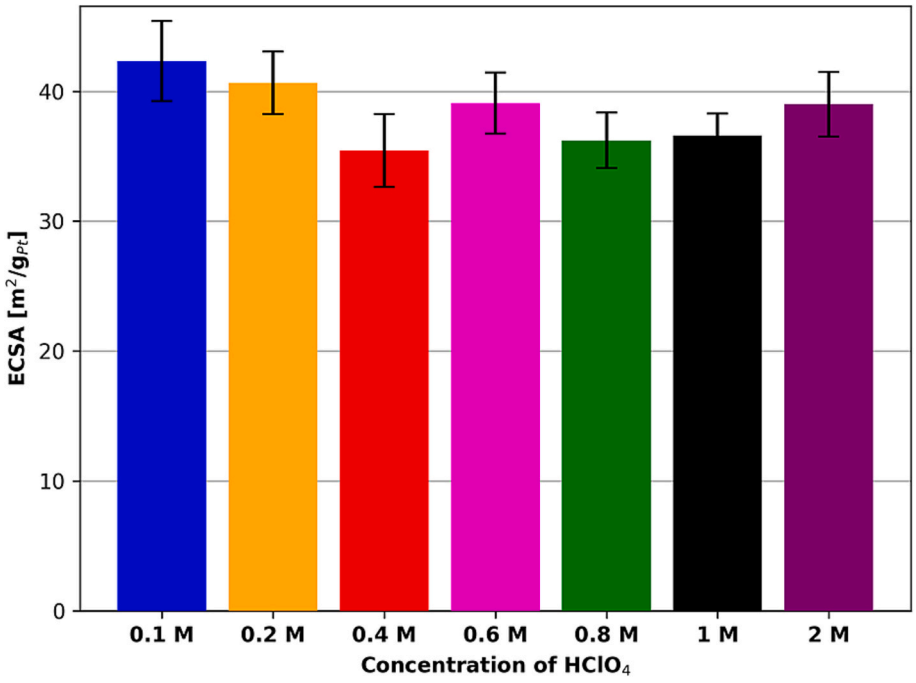

Fig. 2. Electrochemical surface area of Pt/C GDEs determined from H_{upd} voltammetry in different $HClO_4$ concentrations. Data represents three independently prepared electrodes; error bars indicate one standard deviation.

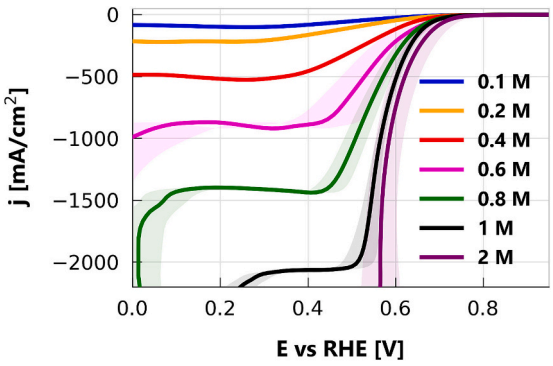

Fig. 3. ORR curves (5 mV s^{-1}) of the samples in different concentrations of $HClO_4$. The curves are 100% iR drop corrected (85% in-situ compensated and 15% post-measurement). Each of the curves is an average of three measured samples, while the shaded region indicates one standard deviation.

electrolyte.

Conclusions

This work provides a systematic comparison of ORR behavior in a GDE setup using 0.1–2 M $HClO_4$. While cyclic voltammetry and ECSA show little dependence on electrolyte concentration, the high-current ORR response changes markedly, with distinct transport-limited plateaus appearing at lower acid concentrations. These results show that proton transport, rather than oxygen supply, limits the maximum achievable current density. Accordingly, at least 0.8 M $HClO_4$ should be used for studies targeting 1 A cm^{-2}, while 2 M $HClO_4$ is required to reach 2 A cm^{-2}.

More broadly, the results show that GDE setups can serve not only for catalyst screening, but also as a platform for probing proton transport limitations under membrane-relevant conditions.

The present study was limited to a single commercial 50 wt% Pt/C catalyst system. Future work should investigate how catalyst-layer parameters such as Pt loading, ionomer content, catalyst-layer thickness, and Pt particle size influence proton transport limitations and the achievable current density in GDE measurements. Future studies should also evaluate how alternative acidic electrolytes and proton-conducting environments influence proton transport limitations in high-current-density GDE measurements. In the proton-transport-limited regime, the limiting current is expected to depend primarily on local proton activity, or surface pH, which is governed by the balance between proton consumption and proton transport. Replacing $HClO_4$ with other electrolytes, such as H_2SO_4, would also change anion adsorption, conductivity and double-layer structure, and would therefore probe acid-identity effects rather than only proton availability.

CRediT authorship contribution statement

Aleš Marsel: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Data curation, Conceptualization. **Miha Hotko:** Writing – review & editing. **Nik Maselj:** Writing – review & editing. **Nejc Hodnik:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ales Marsel reports financial support, equipment, drugs, or supplies, and travel were provided by Johnson Matthey plc. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[1] S. Alinejad, et al., J. Phys. Energy 2 (2020) 024003.

[2] K. Ehelebe, et al., ACS Energy Lett. 7 (2022) 816–826.
[3] D. Van Der Vliet, et al., J. Electroanal. Chem. 647 (2010) 29–34.
[4] J. Omura, H. Yano, D.A. Tryk, M. Watanabe, H. Uchida, Langmuir 30 (2014) 432–439.
[5] N. Markovic, H. Gasteiger, P.N. Ross, J. Electrochem. Soc. 144 (1997) 1591–1597.
[6] M. Luo, M.T.M. Koper, Nat. Catal. 5 (2022) 615–623.
[7] J.A. Zamora Zeledón, et al., ChemElectroChem 8 (2021) 2467–2478.
[8] B.A. Pinaud, A. Bonakdarpour, L. Daniel, J. Sharman, D.P. Wilkinson, J. Electrochem. Soc. 164 (2017) F321–F327.
[9] M. Inaba, et al., Energy Environ. Sci. 11 (2018) 988–994.
[10] G.K.H. Wiberg, M. Fleige, M. Arenz, Rev. Sci. Instrum. 86 (2015) 024102.
[11] Ina Reichmann, Vicent Lloret, Konrad Ehelebe, Pascal Lauf, Ken Jenewein, Karl J. J. Mayrhofer, Serhiy Cherevko, ACS Measurement Science Au 4 (5) (2024) 515–527, https://doi.org/10.1021/acsmeasuresciau.4c00018.
[12] K. Ehelebe, et al., Angew. Chem. Int. Ed. 60 (2021) 8882–8888.
[13] G.A. Attard, A. Brew, K. Hunter, J. Sharman, E. Wright, Phys. Chem. Chem. Phys. 16 (2014) 13689–13698.
[14] N. Hodnik, C. Baldizzone, S. Cherevko, A. Zeradjanin, K.J.J. Mayrhofer, Electrocatalysis 6 (2015) 237–241.
[15] M. Auinger, et al., Phys. Chem. Chem. Phys. 13 (2011) 16384.