Title

Influence of Supporting Electrolyte on Hydroxide Exchange Membrane Water Electrolysis Performance: Catholyte

Permalink

https://escholarship.org/uc/item/51v765xm

Journal

Journal of The Electrochemical Society, 169(2)

ISSN

0013-4651

Authors

Kiessling, Aleksandr
Fornaciari, Julie C
Anderson, Grace
et al.

Publication Date

2022-02-01

DOI

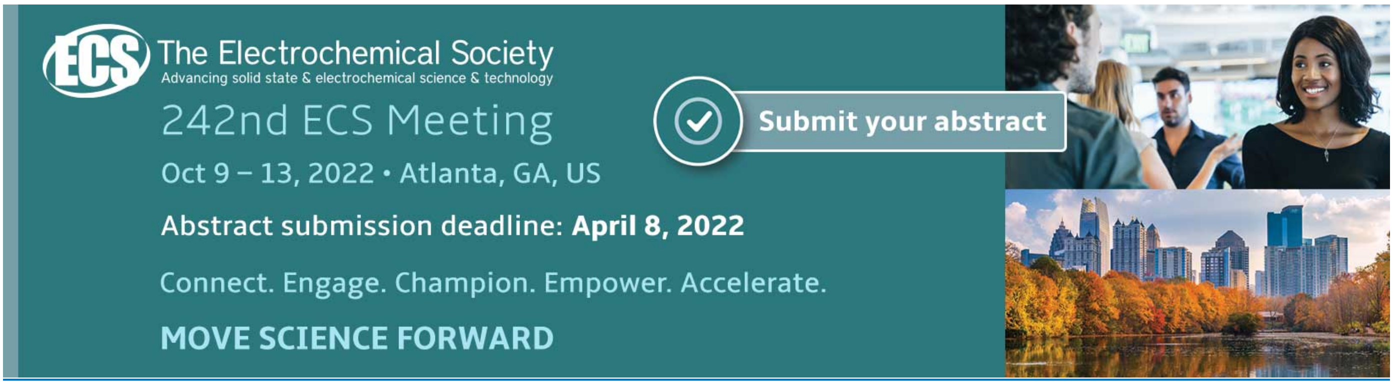
10.1149/1945-7111/ac4fed

Journal of The Electrochemical Society

The Electrochemical Society
Advancing solid state & electrochemical science & technology

Influence of Supporting Electrolyte on Hydroxide Exchange Membrane Water Electrolysis Performance: Catholyte

To cite this article: Aleksandr Kiessling *et al* 2022 *J. Electrochem. Soc.* **169** 024510



Journal of The Electrochemical Society, 2022 **169** 024510

Influence of Supporting Electrolyte on Hydroxide Exchange Membrane Water Electrolysis Performance: Catholyte

Aleksandr Kiessling,[1,2] Julie C. Fornaciari,[1,3] Grace Anderson,[1,3] Xiong Peng,[1] Andreas Gerstmayr,[1,2] Michael Gerhardt,[1] Samuel McKinney,[4] Alexey Serov,[4,*] Adam Z. Weber,[1,] Yu Seung Kim,[5] Barr Zulevi,[4] and Nemanja Danilovic[1,z]**

[1] *Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States of America*
[2] *Technical University of Munich, Department of Chemistry, D-85748 Garching, Germany*
[3] *Departments of Chemical Engineering, University of California Berkeley, Berkeley, California 94720, United States of America*
[4] *Pajarito Powder LLC, Albuquerque, New Mexico 87109, United States of America*
[5] *MPA-11: Materials Synthesis and Integrated Devices, Los Alamos National Laboratory, Los Alamos, New Mexico United States of America*

Alkaline or hydroxide exchange membrane water electrolysis (HEMWE) is a promising technology for green hydrogen production using platinum group metal-free catalysts and stainless steel, an advantage of alkaline water electrolysis (AWE), and a gas-impermeable membrane, a parallel to proton exchange membrane electrolysis (PEMWE). However, the HEMWE requires supporting electrolytes and there is minimal understanding of their role on the respective reactions. Without SELs, HEMWE performance and durability are worse than PEMWE systems. Herein, consistently feeding potassium hydroxide anolyte, we systematically study the effects of catholyte SELs in HEMWEs including dry vs. wet operation, cation effects, anion effects, and cation/OH ratios on cell potential and stability. We report that (i) hydration of the cathode improves high current density operation by preventing dehydration of the hydroxide exchange membrane (HEM), (ii) there was no correlation between cation type and cell potential, (iii) cell potential and high frequency resistance did not correlate with SEL conductivity, (iv) cathodic carbonate SEL had a significant negative effect on cell performance, (v) increased cation/OH ratio also caused increased cell potentials. Overall, this study concludes that feeding water or potassium hydroxide solution is desirable to improve the AEMWE performance.

[DOI: 10.1149/1945-7111/ac4fed]

Manuscript submitted September 23, 2021; revised manuscript received January 3, 2022. Published February 9, 2022.

Supplementary material for this article is available online

Technology enabling long-term energy storage is required in order to transition to a carbon-neutral economy.[1,2] Water electrolysis is a technology, which enables electrochemical conversion of electricity and water into hydrogen, a scalable energy storage medium, and oxygen. However, widespread adoption and use of electrolyzers is contingent on the reduction of capital and operating costs, and thus the price of the produced hydrogen. One approach to reducing capital expenditures is to enable hydroxide exchange membrane water electrolysis (HEMWE), which utilizes cheaper stainless-steel bipolar plates in lieu of the titanium components used in proton exchange membrane water electrolysis (PEMWE).[3–5] Additionally, efficiencies are also improved using HEMWE by enabling the use of thin membranes (25–100 μm) instead of thick diaphragm separators that are used in the established alkaline water electrolysis (AWE).[6–10] A HEMWE, shown in Fig. 1, splits water according to Eqs. 1 and 2.

Hydrogen evolution reaction (HER):

$$4H_2O + 4e^- \rightarrow 4HO^- + 2H_2 \qquad [1]$$

Oxygen evolution reaction (OER):

$$4HO^- \longrightarrow O_2 + 2H_2O + 4e^- \qquad [2]$$

HEMWEs are typically operated with only an anode (anolyte) feed, leveraged from the PEMWE systems, and eases product separation of the hydrogen.[11,12] This dry cathode operation makes sense for PEMWE as the water is required at the anode, however, as shown in Eq. 1, the cathode reaction requires water. For a dry cathode, the water is delivered to the cathode by diffusion from the anode. HEMWE's operated in this manner could become diffusion limited.[13–16] Nevertheless, HEMWEs performance (overpotential) and durability suffer when operating on deionized water (DIW) regardless of configuration, therefore the standard practice is to introduce an SEL with an anolyte feed only.[11]

We recently reported[16] on the effects of the anolyte SEL on HEMWE operation, identified the function of the SEL relative to the alkaline ionomer, and discovered that operation with DIW uses only the catalyst sites covered with the alkaline ionomer. We identified that the optimal anode SEL was potassium hydroxide over potassium bicarbonate due to the carbonation of the HEM. We explicitly operated the cathode in the conventional dry (dead-ended cathode) fashion. Herein we focus on the effects of the catholyte SEL and HER.

Recent progress in the understanding of the alkaline HER mechanism on platinum group metal (PGM) catalysts and the influence of alkali metal cations in aqueous electrolytes using rotating disk electrodes (RDE, half-cell measurements) has shown potential improvements in HEMWE performance.[17–25] As alkali metal cations facilitate hydroxide removal from the interfacial double layer and catalyst surface into the bulk SEL, a high concentration of charge results in accelerated hydroxide removal.[24,26] A performance-enhancing trend in the order of $Li^+ < Na^+ < K^+$ was experimentally verified[27,28] and a ~50% increase in exchange current density was observed for 0.1 M KOH compared to 0.1 M LiOH in RDE with Pt/C.[29] Furthermore, a higher cation to HO^- ratio was found to accelerate hydroxide removal.[24] However, these observations were made in half cell experiments at concentrations of ~0.1 M and it has not been explored whether this can yield overpotential reductions in a HEMWE.

Herein, we attempt to determine the role of the catholyte SELs in the HEMWE by evaluating the following: is the HEMWE performance influenced by catholyte cation or anion effects (hydroxide,

[*] Electrochemical Society Member.
[**] Electrochemical Society Fellow.
[z] E-mail: ndanilovic@lbl.gov

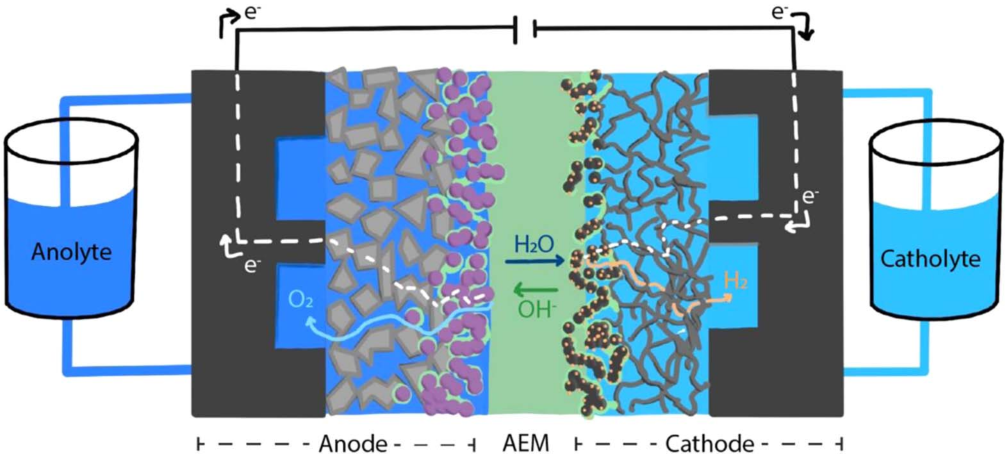


Figure 1. HEMWE sketch; Abbreviations: PTL—porous transport layer, CL—catalyst layer, HEM—alkaline exchange membrane, anolyte—anodic supporting electrolyte, catholyte—cathodic supporting electrolyte. OER is performed in the anode CL and HER in the cathode CL.

carbonate and nitrate)?; is the catholyte SEL conductivity or pH more important for performance?; how do catholyte SELs affect performance vs. water or dry cathode operation? The insights found will be of relevance to the emerging HEMWE community.

Experimental

The same procedures and materials are used in this study as in our catholyte study,[16] for brevity we only provide a brief summary below.

Cell materials and electrolyte solutions.—Tokuyama A201 membrane (28 μm dry thickness) and AS-4 ionomer were used in this study as membrane-electrode assemblies (MEAs) acquired from Pajarito Powder LLC (PP), Albuquerque, NM, USA, and received as catalyst-coated membranes (CCMs). Target catalyst loadings of 2 mg cm^{-2} IrO_2 (~150 m^2 gr^{-1}, PP) and 1 mg cm^{-2} 50 wt% Pt/C (~130 m$_{Pt}^2$ gr^{-1}, PP), and AS-4 ionomer-to-catalyst ratios were 10 and 15 wt% for IrO_2 and Pt/C respectively. CCMs were spray coated using ultrasonic Sono-Tek *ExactaCoat*, although the final loadings varied as reported,[16] importantly catalyst distribution was uniform. Prior to cell testing, MEAs were ion-exchanged to hydroxide form in ~50 ml 1 M KOH at the ambient temperature inside a polyethylene bag for 1 h, rinsed, and then mounted into the cell.

SELs were prepared under ambient conditions using deionized water(DIW, Milli-Q) and solutes, given in Supporting Table I. Electrolyte conductivity and pH were measured using a Thermo Fischer Scientific *Orion Starr A215* pH/conductivity meter with an *Orion 013005MD* conductivity probe and *Orion 8157BNUMD Ross Ultra pH/ATC* triode.

Cell preparation.—The cell used for the experiments with SELs on both the anode and the cathode side was a Fuel Cell Technologies cell which consisted of 5 cm^2 serpentine titanium (anode) and graphite (cathode) flow fields. Platinum-coated titanium porous transport layers (PTL, NEL Hydrogen) were used on the anode and carbon gas diffusion layers (Toray, Fuel Cell Store, Texas, USA) were used on the cathode to help SEL and gas transport to the catalyst layers. Appropriately sized, PTFE gaskets were used for both anode and cathode to assure the adequate active area pressure was applied using a bolt torque of 40 lb·in. For anolyte and catholyte SEL circulation, two KNF (*NFB25 KPOCB-4A*) pumps are used to flow the SELs. The pumps are operated at 5% of maximum pumping power equaling a flow rate of 22 ml min^{-1}. Cells were assembled in ambient air.

Cells were heated using a *Digi-Sense TC6500* temperature control and heater to a temperature of 60 °C. Heating was never applied when the cell was fully dry but only if there was at least DIW or a supporting electrolyte supplied to the anode side. Electrolytes were indirectly preheated by immersing in beakers and using *VWR* heating plates. For all experiments, 1 M KOH was kept constant as an anolyte throughout this study. However, it was replaced with fresh 1 M KOH for each experimental series, since some degree of catholyte permeation to the anode was observed in longer experiments confirmed via pH measurements.

Cell testing.—Biologic *VMP3B*-10 potentiostat was used for electrochemical characterization of the CCMs, which were preconditioned by collecting cyclic voltammograms (CVs) from 1.23 to 2 V at 50 mV s^{-1}. Polarization curves were recorded using 2 min constant current holds, with subsequent EIS measurement. EIS was recorded from 1 MHz to 100 mHz with 6 points per decade according to Supporting Table IV. Data were processed using MATLAB. EIS data was automatically fitted to an R-RQ-RQ circuit using the ZFit MATLAB script found online[30] and the fits achieved good results. The SEL tests run in a sequence: the MEA is tested with anolyte and catholyte 1 M KOH SELs, followed by changes in the catholyte. To evaluate MEA degradation between catholyte changes, 1 M KOH is used as catholyte in between the other electrolytes and its performance was used to quantify degradation. For each of the figures, numbers in parentheses give the series of test execution. We caution that due to the sequential experiment

Table I. Comparison of kinetic overvoltage at 10 mA cm^{-2}.

Catholyte SEL	Overvoltage (mV) at 10 mA cm^{-2}[a)]	SEL conductivity (mS cm^{-1})
Dry	−10	n/a
DIW	−10	0.056
1 M KOH	0	333
1 M NaOH	0	286
1 M LiOH	20	254

a) Relative to KOH in experimental sequence.

execution, the data obtained shows qualitative trends, and HFR between different experimental series should not be compared.

For microelectrode half-cell measurements a Pt (50 um, BASI) microelectrode was used in a miniature 3 electrode electrochemical cell. A commercial HydroFlex DHE was used with a Pt counter electrode. The same electrolyte solutions used in full-cell measurements were used for half-cell measurements, consisting of KOH and K_2CO_3 solutions of varying concentration at 25 °C.

Results and Discussion

***Impacts of flowing cathodic SEL.*—**Typically, membrane-based electrolyzers operate with a no-inlet feed cathode, in order to yield drier hydrogen as a product.[16] However, for alkaline HER (Eq. 1), water is an explicit reactant. Thus, if the water only comes from the anode side through the membrane, the cell performance and durability may be limited by mass transport and HEM dry out.[15] Hypothetically, adding water or supporting electrolytes to the cathode should alleviate any overpotentials that arise from the lack of reactant. Interestingly, the literature does not explore this direction or shows the same or worse performance when feeding in a liquid to the cathode. As shown in Fig. 2, we observe the performance is *similar* (within 10 mV), whether the cell is operated with no catholyte, DIW, or 1 M KOH, while also feeding 1 M KOH on the anode.

Although the difference between the wet (DIW or KOH) and dry cathodes is less than 100 mV at 2 A cm^{-2}, there are important differences. First, in the kinetic region (Fig. 2 inset), the cell is less kinetically limited under dry cathode conditions as opposed to when DIW or 1 M KOH are used as a catholyte. Ascribing this effect solely to the cathode side of the cell, this result implies that neither the local pH nor ionomer hydration seems to impact the HER, consistent with our recent study.[16] Looking at it from a different perspective, the presence of the ions from KOH, presumably in the non-ionomer portions of the cathode catalyst layer, results in polarization resistance and worse kinetics (as discussed in more detail in later sections). At the same time, DIW also has higher overpotential than dry cathode (at low currents). We suspect that these effects are from a small crossover of KOH to the cathode, as we observed a pH increase of the DIW after the test was completed. Up to roughly 750 mA cm^{-2}, the dry cathode MEA performance is better than the dual fed 1 M KOH cell, and better than the DIW up to 1250 mA cm^{-2}. Above ~600 mA cm^{-2}, the ohmic resistance (Fig. 2b) of the dry cathode fed MEA starts to increase resulting in worse performance relative to the DIW or KOH fed MEAs. While the KOH and DIW ohmic resistances continue to decrease with increasing current. This result indicates the onset of possible dehydration behavior of the membrane or ionomer in the dry cathode case or the transition to the KOH being the dominant ion carrier in the non-ionomer phase of the cathode catalyst layer. Feeding DIW at least seems to prevent the increase in HFR due to dehydration, however, further investigation into how the catholyte could help stability and durability needs to be done. Nevertheless, the catholyte may show promising results when the membrane and catalyst layers are actively being stressed at a more constant rate. Furthermore, the catholyte is clearly important, as the cation or anion of choice may still impact the overall performance of the cell.

***Cation effects.*—**We next investigate the effect of cations when flowing a catholyte SEL. We note that we use a highly porous Toray paper cathode GDL that allows for adequate flow of SEL from the flowfield to the catalyst layer on the cathode side of the cell without a microporous layer (similar to what is used in flow batteries). We first investigate whether the kinetics-improving effect of Li^+ and Na^+ compared to K^+ on the HER, observed in rotating disk electrode (RDE) measurements translate to an HEMWE. We further look at the effect of catholyte pH and conductivity on cell performance.

In Fig. 3, we explore the impacts of LiOH (a) and NaOH (b) cations relative to KOH. In the kinetic region, Li^+ had a detrimental effect relative to K^+ (inset), however, it was not apparent in the polarization resistance (SI Fig. 3 (available online at stacks.iop.org/JES/169/024510/mmedia)). The detrimental effect persisted upon reintroduction of KOH between catholyte changes, and the overpotential increased when the concentration was increased. For Na^+ there were no significant observable differences in any region. In all cases K^+, Na^+, and Li^+ containing catholytes, the HFR consistently decreases with current (Fig. 3b and SI Figs. 2 and 3). Table I compares the trends between three cation types. Comparing the catholyte, cation effect, with those found for anolytes[16]; in the kinetic region both Na^+ and Li^+ had negative effects on performance resulting in the following trend: $K^+ < Na^+ < Li^+$. In both anolyte and catholyte cases, the Li^+ impacts the kinetic performance the most by increasing the overpotential by about 20 mV, which we previously concluded to be due to the stabilization of the OH^*. In contrast, in the ohmic region Li^+ containing anolytes in particular, but K^+ and Na^+ also caused a steady increase in HFR at high current densities, without the presence of a catholyte. Overall, in full-cell

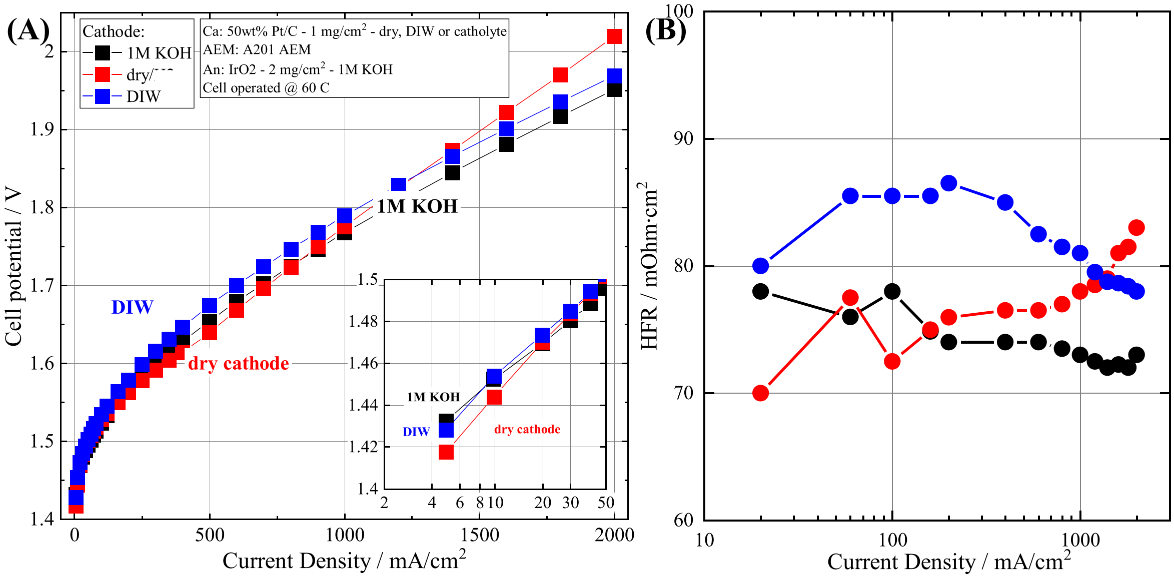


Figure 2. (a) Polarization curve showing kinetic (inset) and ohmic regions and (b) high frequency resistance (HFR) for HEWME operated with dry cathode, deionized water (DIW) or 1 M KOH as the catholyte, with 1 M KOH as analyte in all cases.

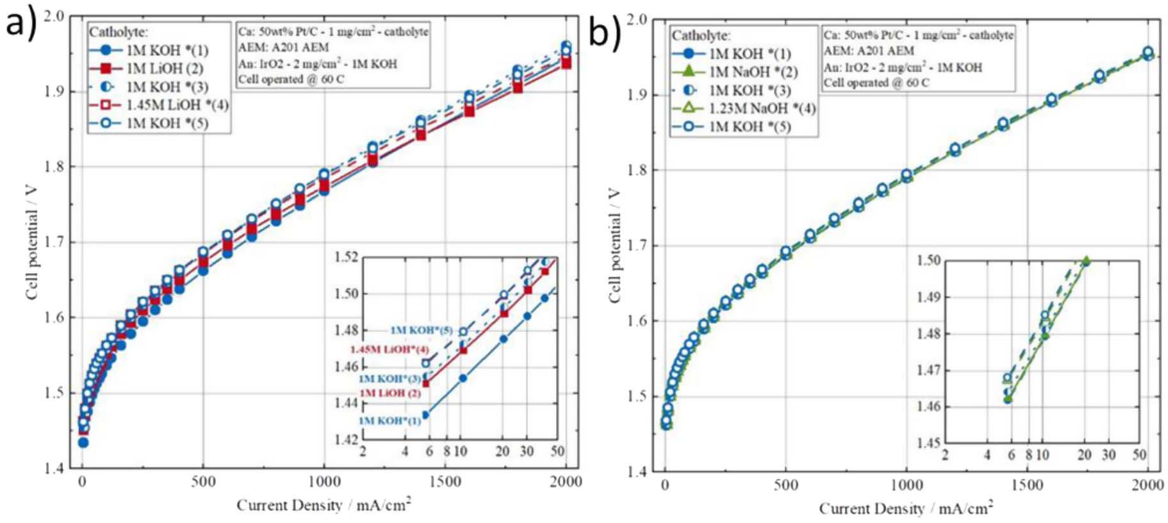


Figure 3. Polarization curves showing kinetic (inset) and ohmic regions for (a) LiOH, (b) NaOH and KOH catholytes. Numbers in brackets indicate the series in which the experiments were conducted consecutively, * denotes similar conductivities at 60 °C.

tests the catholyte SEL cation influence on the HER is not as clear as it was relative to the OER, however, if we consider that relative to dry cathodes, the presence of any cations does negatively influence the HER kinetics, and the trend is $K^+ \sim Na^+ < Li^+$. The decreasing HFR with current density, in all SEL cases, could be an indication that the catholyte SEL does serve to hydrate or overcome some limitations resulting from relying solely on anolyte SEL for water management and reactant supply, which is aggravated at higher current densities due to electroosmotic drag towards the anode. A secondary effect could be in hydroxide diffusion and electroosmotic drag from the catholyte to the anolyte, which we found to over time lead to an increase in the anolyte pH. As seen previously, increasing pH or conductivity of the anolyte results in improved HFR and cell performance.[16,31]

Anion Effects.—Next, we investigate the effects of the catholyte anions on cell performance, between KOH and K_2CO_3 at the same pH and at the same electrolyte conductivity in Fig. 4. In the kinetic region in Fig. 4 (inset), distinct differences (less than 10 mV) in potential are not observed, regardless of hydroxide or carbonate-containing SEL. However, at higher current densities the polarization resistance for carbonate-containing SEL increases compared to hydroxide, indicating that there is something with these carbonate SELs that is impeding the HER or the reactant supply. Examining the HFR in Fig. 4b, the carbonate SEL has a significantly higher HFR at low current density, even compared to the 18 mM KOH, which has a much lower solution conductivity than 0.82 M K_2CO_3. However, the carbonate solution's HFR decreases and approaches that of hydroxide SELs at high current density. Overall, the poorer performance with CO_3^{2-} catholyte is a result of a combination of higher HFR and polarization resistance. These results are starkly different from our findings with anolyte SELs, where K_2CO_3 had shown better performance at higher current densities and at the same SEL pH. These results support a previous modeling study, indicating that the catholyte carbonate presence allows more carbonate to ion-exchange into the HEM initially increasing the HFR.[16,31,32] At higher current densities self-purging, when the carbonates in the HEM are replaced with hydroxide, occurs and results in a lower HFR.

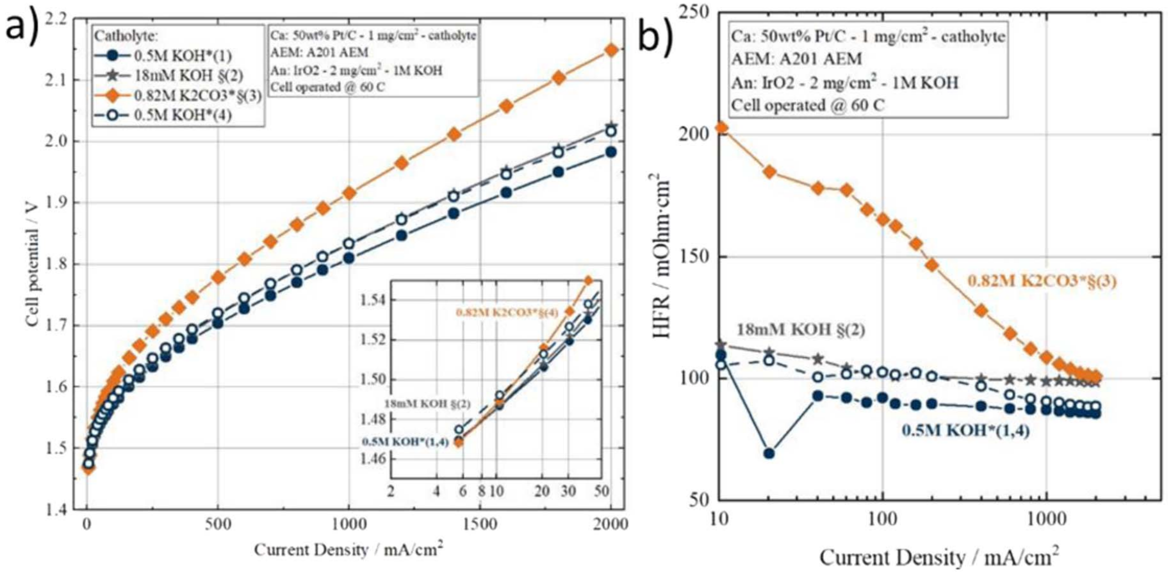


Figure 4. (a) Polarization curves for kinetic (inset) and ohmic regions and (b) HFR; for K_2CO_3 and KOH catholytes. Numbers in brackets indicate the series in which the experiments were conducted consecutively, § denotes similar pH, * denotes similar conductivities at 60 °C.

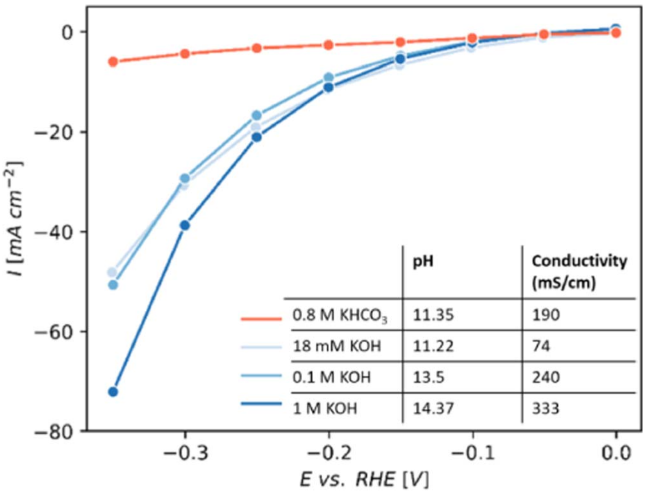


Figure 5. Pt (50 um, BASI) microelectrode half-cell measurements in KOH and K_2CO_3 solutions of varying concentration at 25 °C. Indicating that carbonates are uniquely bad for HER compared to any hydroxide containing electrolyte, regardless of solution conductivity or pH.

We note that decreasing the pH and the conductivity of the SEL by changing the KOH concentration, resulted in a decrease in cell performance due to higher HFR. Which indicates some effect on the membrane conductivity, anolyte dilution or carbonate contamination. With respect to the electrode kinetics, one would expect a decrease in performance at low pH, however, observations for the kinetic region do not align with expectations. Further due to the kinetics-improving effect of the cations, identified in half-cell measurements,[27,29] one would have expected that K_2CO_3 performed better than 18 mM KOH because of the higher cation/OH ratio.

To further elucidate these effects, we performed microelectrode-based half-cell measurements in carbonate and hydroxide solutions on a Pt metal microelectrode, shown in Fig. 5. In these measurements, no alkaline ionomer is present and the kinetic response of Pt in varying solutions can be examined at relatively high current densities, similar to the full-cell measurements we performed. The HER activity was found to be primarily controlled by the presence of hydroxide vs. carbonate. In the carbonate solution, the HER was deactivated. Interestingly, when compared to KOH solutions of similar pH (pH 11–14) and conductivity, the HER was still active. Pt was HER active in KOH across the pH range and solution conductivity tested. Thus, for instance, even though 18 mM KOH and 0.8 M K_2CO_3 had the same solution conductivity, the HER activity of Pt is much higher in the KOH electrolyte. These results suggest that the full-cell findings for carbonate and cation/OH ratio point to a kinetic effect, even though in full-cell tests it was only seen in the polarization resistance at higher current densities. We conclude that in full-cell tests, the cathode ionomer covered sites must provide alternative active sites that are adequate at low current densities, that are protected from the anion effect. To support high current densities the non-ionomer covered sites contribute with a polarization penalty.

Influence of cation/OH ratio and inert anions.—Finally, we investigate whether changing the catholyte cation/OH ratio influences performance, by adding KNO_3, an inert anion, to 18 mM KOH.[16] The pH remained constant while the cation/OH ratio and conductivity increased, while the overall concentration of hydroxide species stayed the same throughout this experiment shown in Fig. 6.

Comparing the polarization curves in Fig. 6, it is evident that increasing the cation/OH ratio of the catholyte is detrimental to cell performance, similar to adding bicarbonate. In Fig. 6a, the kinetic region (inset) shows consistent overpotentials (less than 10 mV difference), indicating no kinetic effect at low current. However, at higher current densities, the polarization resistance is much worse at the higher cation/OH ratio (SI Fig. 9). In other words, there does not appear to be a positive cation effect of catholyte SELs in full-cells, as anticipated based on half-cell studies.[17–21,23,25] Figure 6b is more definitive, showing higher HFR values with increasing cation/OH ratios, although the catholyte solution conductivity was increasing with the addition of KNO_3 from 7.6 to 21.5 to 70.5 mS/cm, respectively. Consequently, cell performance did not correlate with catholyte conductivity. We summarize the SEL conductivities and cell HFR in Table II for various catholytes investigated to reinforce this point. Lastly, with increasing current density the nitrate is self-purged through the HEM towards the anode side of the cell. Higher initial HFR and subsequent decrease with increasing current density can be attributed to the presence and purging of NO_3^- (similar to CO_3^{2-} above).

The increased cation/OH ratio could provide insight into when these HEMWEs are operating for longer durations. Cations can migrate across to the cathode, even if the cathode is operated in the dry state.[16] If these cations migrate, higher overpotentials can be induced over time. Durability tests would need to be conducted to confirm if the cation/OH ratio changes over time, but with these preliminary findings, the complex nature of ion movement within HEMWEs can play a huge role within the cell.

Conclusion

Herein, we report the results of a detailed catholyte investigation in a HEMWE setup. We performed experiments with catholyte SELs containing different cations and anions while keeping the anolyte SEL constantly at 1.0 M KOH. We observed that there was a beneficial effect of flowing DIW or KOH on the cathode at higher current densities as a result of decreasing HFR. At low current densities, we observed that the presence of cations and anions at the HEM cathode negatively affect HER kinetics although the sensitivity is not as impactful in some cases as it is on the HEM anode. However, changing anions from OH^- to CO_3^{2-} or NO_3^{2-}, we did find a strong negative influence on the overall cell performance, which is attributed to the increased HFR and anion poisoning of the HER catalysis. In both nitrate and carbonate cases, at high current density the anion is self-purged out of the HEM and reduces cell resistance, however some residual cell degradation was observed.

From an operational point of view, a catholyte feed consisting of pure, concentrated KOH or DIW would be a best practice for long-term durability based on the hydrating effects on the HEM. The use of carbonates or other cation electrolytes either resulted in poorer performance or a combination of potential decay or deactivation at operating current densities.

Acknowledgments

A.K. gratefully acknowledges funding from the German Fulbright Commission and the Studienstiftung des deutschen Volkes. A.K. thanks the Office for International Education for continuous support during this stay in the US and Prof. Hubert Gasteiger for fruitful discussions. N.D., M.R.G., X.P., A.Z.W., J.C. F., Y.S.K. and G.A. gratefully acknowledge research support from the HydroGEN Advanced Water Splitting Materials Consortium, established as part of the Energy Materials Network under the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office, under Contract Number DE-AC02–05CH11231 (LBNL) and 89233218CNA000001 (LANL). JCF thanks the National Science Foundation (grant DGE1106400) for support. S.M., B.Z. and A.S. also acknowledge Advanced Research Projects Agency-Energy under contract DE-AR000688. The authors would like to thank Nel Hydrogen for supplying titanium porous transport layers.

ORCID

Julie C. Fornaciari https://orcid.org/0000-0002-0473-2298
Grace Anderson https://orcid.org/0000-0002-2723-5024

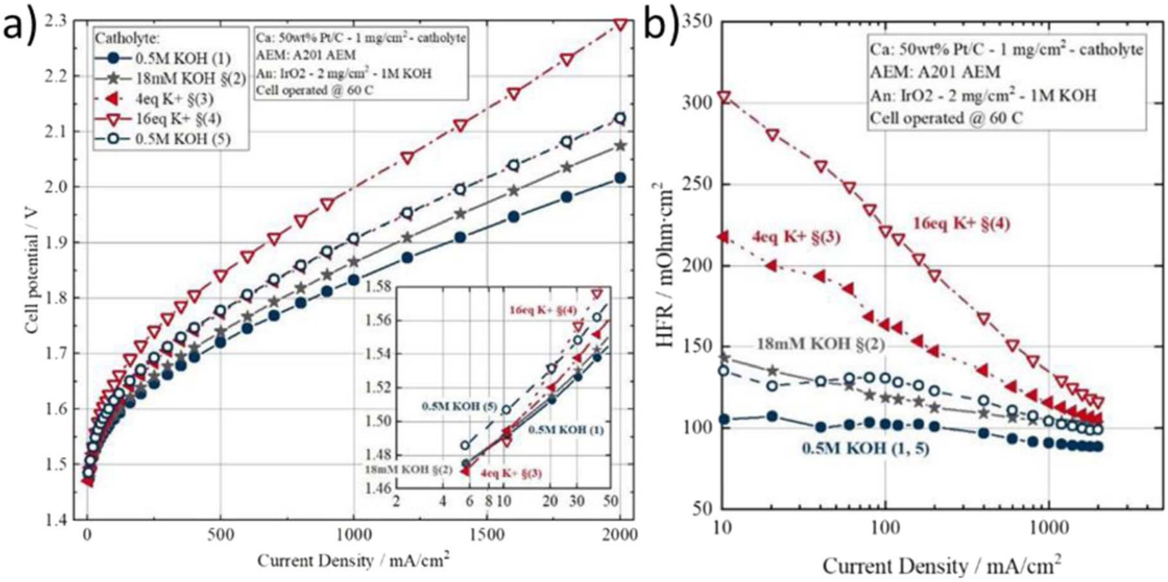


Figure 6. (a) Polarization curves showing kinetic (inset) and ohmic regions and (b) HFR; for KOH + KNO_3 and KOH catholytes. Numbers in brackets indicate the series in which the experiments were conducted consecutively, § denotes similar pH at 60 °C.

Table II. Comparison of SEL conductivity, kinetic overvoltage at 10 mA cm^{-2}, full-cell HFR at 100 mA cm^{-2} and 1 A cm^{-2}.

Cathode SEL	SEL Conductivity (mS cm^{-1})	Cell Voltage (V) at 1 A cm^{-2}	HFR at 1 A cm^{-2} (mOhm cm^2)
Dry	5.5 x 10^{-5}	1.83	84
0.5 M KOH	190	1.79	83
18 mM KOH	7.4	1.84	110
0.82 M K_2CO_3	190	1.92	115
4 eq K^+ (NO_3^-)	21.5	1.9	125
16 eq K^+ (NO_3^-)	70.5	2.0	140

Xiong Peng https://orcid.org/0000-0001-8737-5830
Michael Gerhardt https://orcid.org/0000-0002-1272-3607
Alexey Serov https://orcid.org/0000-0003-3182-4726
Adam Z. Weber https://orcid.org/0000-0002-7749-1624
Yu Seung Kim https://orcid.org/0000-0002-5446-3890
Barr Zulevi https://orcid.org/0000-0003-1696-945X
Nemanja Danilovic https://orcid.org/0000-0003-2036-6977

References

1. R. Abbasi et al., *Adv. Mater.*, **31**, 1805876 (2019).
2. M. Felgenhauer and T. Hamacher, *Int. J. Hydrog. Energy*, **40**, 2084 (2015).
3. Q. Xu, S. Z. Oener, G. Lindquist, H. Jiang, C. Li, and S. W. Boettcher, *ACS Energy Lett.*, **6**, 305 (2021).
4. Z. Zakaria and S. K. Kamarudin, *Int. J. Energy Res.*, **45**, 18337 (2021).
5. H. Andrew Miller, K. Bouzek, J. Hnat, S. Loos, C. Immanuel Bernäcker, T. Weißgärber, L. Röntzsch, and J. Meier-Haack, *Sustain. Energy Fuels*, **4**, 2114 (2020).
6. M. Schalenbach, *Int. J. Electrochem. Sci.*, 1173 (2018).
7. I. Vincent and D. Bessarabov, *Renew. Sustain. Energy Rev.*, **81**, 1690 (2018).
8. W. E. Mustain, *Curr. Opin. Electrochem.*, **12**, 233 (2018).
9. M. R. Kraglund, M. Carmo, G. Schiller, S. A. Ansar, D. Aili, E. Christensen, and J. O. Jensen, *Energy Environ. Sci.*, **12**, 3313 (2019).
10. M. David, C. Ocampo-Martínez, and R. Sánchez-Peña, *J. Energy Storage*, **23**, 392 (2019).
11. D. Li, A. R. Motz, C. Bae, C. Fujimoto, G. Yang, F.-Y. Zhang, K. E. Ayers, and Y. S. Kim, *Energy Environ. Sci.*, **14**, 3393 (2021).
12. C. C. Pavel, F. Cecconi, C. Emiliani, S. Santiccioli, A. Scaffidi, S. Catanorchi, and M. Comotti, *Angew. Chem. Int. Ed.*, **53**, 1378 (2014).
13. H. Ito, N. Kawaguchi, S. Someya, T. Munakata, N. Miyazaki, M. Ishida, and A. Nakano, *Int. J. Hydrog. Energy*, **43**, 17030 (2018).
14. I. Vincent, A. Kruger, and D. Bessarabov, *Int. J. Hydrog. Energy*, **42**, 10752 (2017).
15. J. C. Fornaciari, M. R. Gerhardt, J. Zhou, Y. N. Regmi, N. Danilovic, A. T. Bell, and A. Z. Weber, *J. Electrochem. Soc.*, **167**, 104508 (2020).
16. A. Kiessling et al., *J. Electrochem. Soc.*, **168**, 084512 (2021).
17. J. Durst, A. Siebel, C. Simon, F. Hasché, J. Herranz, and H. A. Gasteiger, *Energy Environ. Sci.*, **7**, 2255 (2014).
18. Q. Jia, E. Liu, L. Jiao, J. Li, and S. Mukerjee, *Curr. Opin. Electrochem.*, **12**, 209 (2018).
19. S. Intikhab, J. D. Snyder, and M. H. Tang, *ACS Catal.*, **7**, 8314 (2017).
20. S. Intikhab, L. Rebollar, X. Fu, Q. Yue, Y. Li, Y. Kang, M. H. Tang, and J. D. Snyder, *Nano Energy*, **64**, 103963 (2019).
21. I. Ledezma-Yanez, W. D. Z. Wallace, P. Sebastián-Pascual, V. Climent, J. M. Feliu, and M. T. M. Koper, *Nat. Energy*, **2**, 972 (2017).
22. N. Danilovic, R. Subbaraman, D. Strmcnik, K.-C. Chang, A. P. Paulikas, V. R. Stamenkovic, and N. M. Markovic, *Angew. Chem.*, **124**, 12663 (2012).
23. L. Rebollar, S. Intikhab, J. D. Snyder, and M. H. Tang, *J. Electrochem. Soc.*, **165**, J3209 (2018).
24. E. Liu, J. Li, L. Jiao, H. T. T. Doan, Z. Liu, Z. Zhao, Y. Huang, K. M. Abraham, S. Mukerjee, and Q. Jia, *J. Am. Chem. Soc.*, **141**, 3232 (2019).
25. B. Xu, J. Zheng, Y. Yan, Z. Zhuang, and W. Sheng, *Sci. Adv.*, **2.3**, e1501602 (2016).
26. E. Liu, L. Jiao, J. Li, T. Stracensky, S. Mukerjee, and Q. Jia, *Energy and Environmental Science*, **13**, 3064 (2020).
27. S. Xue, B. Garlyyev, S. Watzele, Y. Liang, J. Fichtner, M. D. Pohl, and A. S. Bandarenka, *ChemElectroChem*, **5**, 2326 (2018).
28. N. Danilovic, R. Subbaraman, D. Strmcnik, A. P. Paulikas, D. Myers, V. R. Stamenkovic, and N. M. Markovic, *Electrocatalysis*, **3**, 221 (2012).
29. D. J. Weber, M. Janssen, and M. Oezaslan, *J. Electrochem. Soc.*, **166**, F66 (2019).
30. J.-L. Dellis, ZFIT Funct. Which Can PLOT SIMULATE FIT Impedance Datahttps://de.mathworks.com/matlabcentral/fileexchange/19460-zfit.
31. J. Liu, Z. Kang, D. Li, M. Pak, S. M. Alia, C. Fujimoto, G. Bender, Y. S. Kim, and A. Z. Weber, *J. Electrochem. Soc.*, **168**, 054522 (2021).
32. L. N. Stanislaw, M. R. Gerhardt, and A. Z. Weber, *ECS Trans.*, **92**, 767 (2019).