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Review Article
Impact of ionomer adsorption on alkaline hydrogen oxidation activity and fuel cell performance

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The adsorption of the ionomer components significantly impacts the activity of hydrogen oxidation reaction (HOR) catalysts under high pH conditions. Two specific adsorptions, i.e., (i) cation-hydroxide-water co-adsorption and (ii) phenyl group adsorption, on the surface of platinum group metal HOR catalysts were identified as the performance-limiting factors for anion-exchange membrane fuel cells (AEMFCs). Here, we review the main characteristics of the surface adsorptions, their impact on the performance of HOR half-cell and AEMFC, and the mitigation strategies. This review emphasizes important aspects in the design of electrocatalysts and ionomers for improved AEMFC performance.

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Introduction

Alkaline anion-exchange membrane fuel cells (AEMFCs) is an attractive alternative to acidic proton-exchange membrane fuel cells (PEMFCs) due to the potential use of inexpensive non- platinum group metal (PGM) catalysts [1]. At the early stage of the development, low hydroxide conductivity and chemical instability of anion exchange membranes (AEMs) were the main hurdles for AEMFC technology. As highly conductive and stable AEMs and soluble ionomer dispersions were developed in the early 2010s [2–5], membrane electrode assemblies (MEAs) were fabricated; however, the performance of the AEMFCs was low, ca. the peak power density of $< 200\,mW\,cm^{-2}$ [6].

Yang *et al.* [7] suggested that a possible reason for the low AEMFC performance is the slow hydrogen oxidation reaction (HOR) kinetics on the catalysts. Consequently, the research focus diversified to develop highly active HOR catalysts and to understand HOR mechanistic aspects [8–11,12•], which have drawn substantial attention and often used to discuss improved AEMFC performance. For example, Zhuang *et al.* [13] explained their $1\,W\,cm^{-2}$ peak power density of an AEMFC using a HOR mechanistic viewpoint.

Over the last few years, Varcoe *et al.* [14–16•] reported excellent AEMFC performance, $\sim 2\,W\,cm^{-2}$ peak power density, using commercially available HOR catalysts. For those highly performing AEMFC cells, the relatively low HOR activity of the catalysts appears to be no longer the critical performance-limiting factor. Instead, Mustain *et al.* [15,17] suggested that the improved AEMFC performance may be due to the better water management in the cell. However, it seemed that the water management is not the only reason for the excellent performance due to the following reasons: (i) even their cell having poor water management exhibited $\sim 800\,mW\,cm^{-2}$ peak power density while most other AEMFCs employing various polymer electrolytes showed a low peak power density of $< 500\,mW\,cm^{-2}$ [18–22], (ii) the excellent AEMFC performance they presented strongly depends on the electrode ionomer rather than the AEM [23], and (iii) a clear correlation between electrode water transport properties and AEMFC performance was missing.

Another possible performance-limiting factor of AEMFCs is the undesirable adsorption of ionomer on the surface of the HOR catalysts [12,24,25], which has been largely ignored in the research community. **Figure 1** shows examples of the orientation of adsorbed ionomer components on catalyst surface and their adsorption energy on Pt(111) surface. In this review, we summarize the characteristics of two surface adsorptions, i.e., (i) cation-hydroxide-water co-adsorption and (ii) phenyl adsorption. The impact of the adsorptions on the performance of

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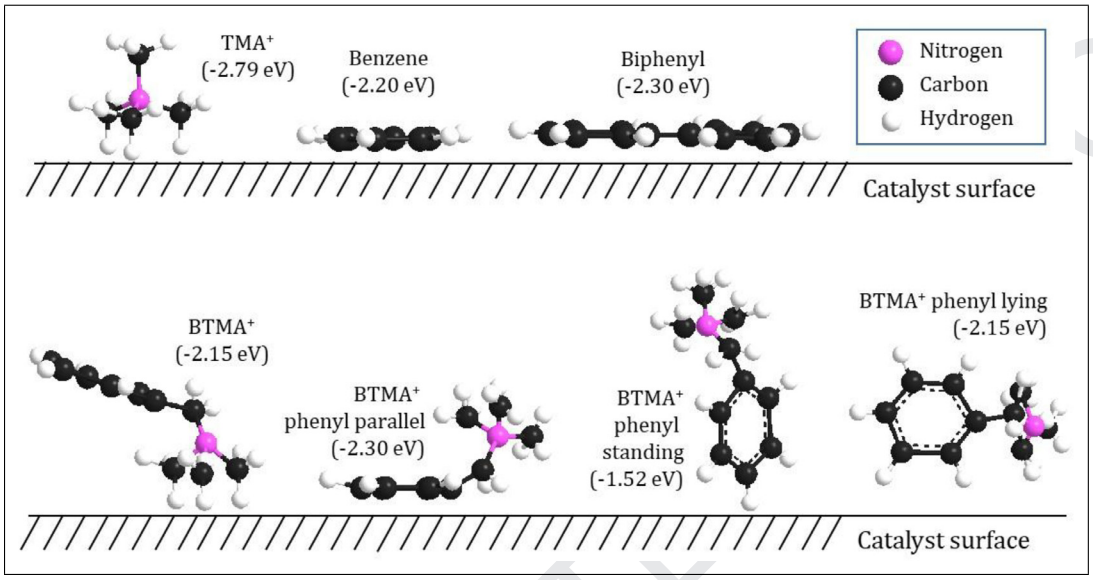
Figure 1



Cartoon showing the orientation of adsorbed ionomer components, tetramethyl ammonium cation (TMA^+), benzene, biphenyl and benzyltrimethyl ammonium cation ($BTMA^+$) on catalyst surface. Numbers in parenthesis denote the adsorption energy of the molecule on Pt(111) calculated from density functional theory (DFT) [26].

HOR half-cell and AEMFC is discussed with reported mitigation strategies.

Cation-hydroxide-water co-adsorption

Kohl *et al.* [27•] were first to observe adsorption of TMA^+ on the Pt surface, which lead to the decreased active surface area of the catalyst and lower rate of methanol oxidation. DFT calculation by Janik *et al.* [28••,29] showed that the Pt hydrogen and hydroxide adsorption peaks in cyclic voltammogram shifted to higher potentials due to the cation-hydroxide-water co-adsorption. Chung *et al.* and Xu *et al.* [30••,31] provided spectroscopic evidence of the co-adsorbed species using infrared reflection absorption spectroscopy. Two notable characteristics of cation-hydroxide-water co-adsorption are as follows: (i) the co-adsorption decreased as the cell potential increased. Complete desorption of cations from Pt electrode did not happen until the electrode was exposed to high potential, i.e., 1.4 V_{RHE} [32] and (ii) the co-adsorption is cumulative. The time-dependent behavior of co-adsorption observed in neutron reflectometry experiment [33] showed that the thickness of the co-adsorbed layer gradually increased to 15 Å after exposure for 10 h at 0.1 V_{RHE}.

Figure 1a shows the effect of cation-hydroxide-water co-adsorption on HOR voltammogram of Pt electrode [30]. The initial HOR voltammogram obtained from the anodic scans [−0.1–1.2 V_{RHE}] in hydrogen-saturated 0.1 M tetramethylammonium hydroxide (TMAOH) solution changed significantly after applying 0.1 V_{RHE} to the Pt electrode for 15 min. Note that both kinetic current density at 0.01 V and the HOR diffusion limiting current density measured at 0.6 V decreased. As the co-adsorption changes the voltammetric behavior of HOR catalysts, a well-designed test protocol is required to obtain consistent HOR voltammograms under alkaline conditions [34•]. Several test protocols have been implemented [8,9,32]. More rigorous high potential preconditioning may be more efficient to remove the co-adsorbed layer from the catalyst surface, yet such process may accelerate the catalyst degradation. Furthermore, even with the rigorous high potential preconditioning, cumulative co-adsorption is unavoidable during the measurement. Thus, the accurate measurement of HOR catalyst activity may still be difficult by HOR voltammetry. Figure 1b explains the HOR inhibition mechanism of the co-adsorption on Pt by the electrochemical impedance spectra collected before and after holding the Pt electrode at 0.1 V_{RHE} for 15 min. The impedance spectra are composed of two semi-circles: one large semi-circle at low frequencies (0.1−400 Hz) and the other small semi-circle at high frequencies (400 Hz−100 kHz). The appearance of two semi-circles for Pt electrode under alkaline conditions is consistent with the previous observation by Koper *et al.* [35]. After the co-adsorption occurred, the size of the semi-circle at high frequencies was invariant, while the size of the semi-circle at low frequencies significantly increased. This result indicates that the inhibition by the co-adsorption is related to the low-frequency semi-circle. The impedance spectra as a function of rotating speed

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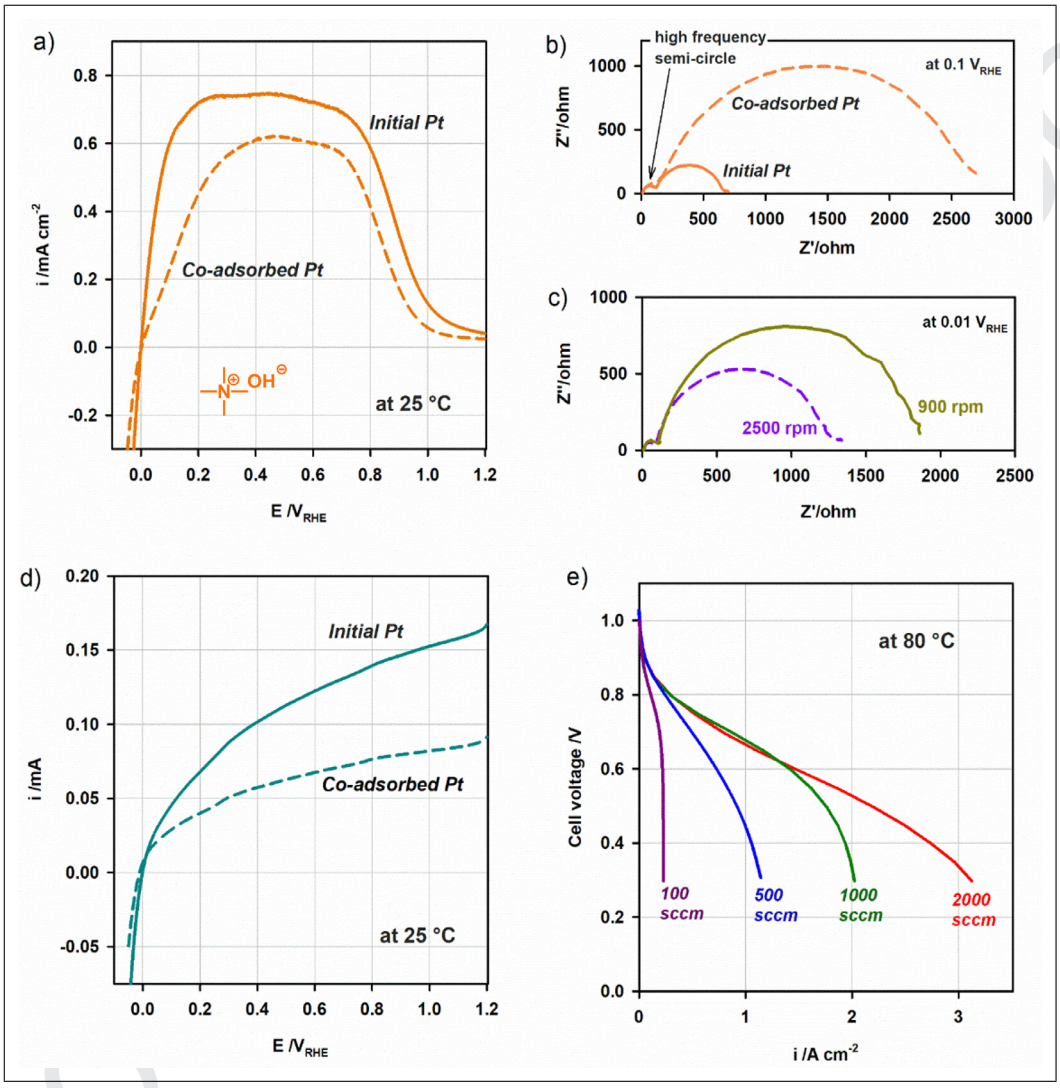
Figure 2



(a) HOR voltammograms of Pt in 0.1 M TMAOH. The voltammograms of Pt were obtained before and after applying 0.1 V_{RHE} to Pt electrode for 15 min. The voltammograms were measured at 25 °C, rotating speed of 900 rpm and scan rate of 5 mV s^{-1}. (b) Impedance spectra of Pt in 0.1 M TMAOH before and after applying 0.1 V_{RHE} for 15 min. The impedance spectra was measured at 0.1 V_{RHE} with the frequency range of 100 kHz to 0.1 Hz. (c) Impedance spectra of Pt in 0.1 M TMAOH before applying 0.1 V_{RHE} for 15 min at 900 and 2500 rpms. The impedance spectra was measured at 0.01 V_{RHE} with the frequency range of 100 kHz to 0.1 Hz. Adapted with permission from *J. Phys. Chem. Lett.* 7, 4464-4469 (2016). Copyright © 2016 American Chemical Society. (c) HOR voltammograms of Pt/C in contact with quaternized poly(biphenylene). The voltammograms were measured by microelectrode half-cell at 25°C before and after applying 0.1 V_{RHE} to Pt electrode for 30 min. (e) The impact of anode flow rate on AEMFC performance. The performance was measured at 80°C at 287 kPa backpressure. AEM (thickness): quaternized poly(terphenylene) (35 μm), ionomer: dimethyl biphenylene (BPN), anode catalyst (loading): PtRu/C (0.75 mg_{metal} cm^{-2}) cathode catalyst (loading): Pt/C (0.6 mg_{metal} cm^{-2}), cathode flow rate: 300 sccm of O_2.

showed that the semi-circle at low frequencies originated from a diffusion-controlled process (**Figure 1c**). The analysis suggested that the co-adsorption causes hydrogen diffusion problem [30] rather than blocking the catalyst active sites or alternating the structure of adsorbed hydroxyl group [36]. The H_2 diffusion-related HOR inhibition looks counterintuitive since H_2 is a small molecule and the diffusion of H_2 is fast. However, it may happen at high hydroxide concentrated co-adsorbed layer in which H_2 solubility and diffusivity substantially decreases [37].

The HOR inhibition by the co-adsorption was also observed in Pt/C in contact with ionomer. **Figure 1d** shows HOR voltamograms of Pt/C in contact with TMA functionalized poly(biphenylene) (BPN). The HOR activity of Pt/C is notably decreased after applying 0.1 V_{RHE} to the

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Pt/C electrode for 30 min. In AEMFCs, the cumulative co-adsorption occurs during the catalyst break-in process within a few hours and it causes hydrogen mass transport issue as the H_2 diffusion through the co-adsorbed layer is slow. **Figure 1e** demonstrates AEMFC performance of an MEA, which shows that the AEMFC performance gradually increases as the anode flow rate increases. The effect of anode flow rate on AEMFC performance is general for the MEAs using TMA functionalized ionomers: reported peak power density of 4–5 cm^2 MEAs with an anode flow rate of ≥ 1.0 L min^{-1} is ≥ 1.5 W cm^{-2} [38–40•], with an anode flow rate of 0.4 L min^{-1} is 0.6–1.0 W cm^{-2} [13], with an anode flow rate of 0.25 L min^{-1} is 0.36 W cm^{-2} [41], and with an anode flow rate 0.1 L min^{-1} is ~ 0.2 W cm^{-2} [42–44]. The mitigation strategies of the co-adsorption include (i) using a catalyst with less cation adsorbed characteristics [45] and (ii) using ionomers with cations that adsorb weakly on the catalyst. Bulky cations such as tetraethylammonium have a smaller adsorption energy than TMA [31,46]. Therefore, replacing TMA cationic group with bulky cationic groups can effectively mitigate the impact of the undesirable co-adsorption.

Phenyl adsorption

The adsorption of benzene on the surface of the metal catalyst in alkaline and acidic solutions has been extensively investigated over the past several decades using cyclic voltammetry, electrochemical mass and infrared spectroscopy, and radiotracer methods [47–52]. However, the adverse impact of phenyl adsorption on HOR catalysts has not been a significant issue for PEMFCs in which phenyl-free perfluorinated ionomers such as Nafion have been used. On the other hand, for AEMFCs, it is critically important to understand the effect of phenyl adsorption to improve the performance because no alkaline-stable and phenyl-free polymer electrolytes are available yet. A recent study [53••] showed that the adsorption of the phenyl group in quaternized ionomers lowers the HOR activity of Pt catalyst. Two distinctive features of phenyl adsorption over the cation-hydroxide-water co-adsorption were noted from this research; (i) the phenyl adsorption is not cumulative, indicating that the phenyl group is physisorbed by the interaction of aromatic π-electrons of phenyl with the electronic cloud around the metal atoms and (ii) the co-adsorption impacts the HOR voltammogram and AEMFC performance by blocking the active sites of the catalyst without H_2 diffusion issue.

Figure 3a compares the HOR voltammograms of Pt/C in 0.1 M TMAOH and benzyl trimethyl ammonium hydroxide (BTMAOH). Note that the current density of the HOR voltammogram of Pt/C in 0.1 M BTMAOH drops at ~ 0.03 V_{RHE} and then starts to increase again at 0.06 V_{RHE} before reaching the diffusion limiting current at ~ 0.3 V_{RHE}. DFT calculation data indicate that the HOR current loss at ~ 0.03 V_{RHE} is due to the phenyl group adsorption parallel to the Pt surface and that the recovered HOR current at the higher potentials is due to the configurational change from phenyl group adsorption to ammonium group adsorption which is more favorable at high electric field. The phenyl group adsorption decreases in the case of Pt bimetallic alloys. **Figure 3b** shows the HOR voltammogram of several Pt bimetallic alloys in 0.1 M BTMAOH. The current density inflection point observed in the Pt/C catalyst was reduced in Pt bimetallic alloys [53]. The projected density of states calculated using DFT indicates that alloying Pt with Mo, Ni, and Ru pushes the center of the *d*-band of surface Pt atoms toward more negative values relative to the Fermi level, which increases filling of antibonding orbitals between phenyl molecular orbitals and the metal surface [54] and decreases the adsorption energy of BTMA on the alloyed catalysts. The effect is the most pronounced with PtRu followed by PtNi and PtMo. Another approach to reducing the phenyl group adsorption is introducing a non-rotatable phenyl group [40] or bulky cation [55] in the polymer backbone. DFT calculations [40] show that the barrier to rotation around the phenyl-phenyl bond in biphenyl is relatively small, which causes this fragment to adsorb strongly on the HOR catalysts. On the other hand, non-rotatable phenyl groups such as fluorene have significantly lower adsorption energy than biphenyl groups.

Figure 3c and d illustrate the impact of phenyl adsorption at the catalyst-ionomer interface on HOR voltammogram and AEMFC performance, respectively [56]. **Figure 3c** shows HOR voltammograms of Pt/C in contact with BTMA functionalized poly(phenylene) (PP-BTMA). The HOR activity of Pt/C is substantially depressed till 0.6 V_{RHE} and gradually recovered as the cell voltage increased to 0.8 V_{RHE}. The higher recovering potential is a distinct difference from the alkaline liquid electrolyte for which the HOR current recovers at 0.3 V_{RHE}. That is likely because the cation-unsubstituted phenyl groups in the polymer backbone are unable to desorb from the catalyst surface by the configurational change. Unpublished DFT calculations show that the adsorption energy of the polymer backbone fragment 1,2-biphenyl benzene is smaller than that of biphenyl, but its coverage is much larger thus the adverse impact of the phenyl groups in the polymer backbone can still be significant. The HOR activity improved with a PtRu/C catalyst when used with the same ionomer. Further improvement of HOR activity was obtained with a less phenyl group containing poly(phenylene) (PPA-HTMA) and a less phenyl group adsorbing poly(fluorene) (FLN) ionomers (**Figure 3a**). **Figure 3d** shows that the AEMFC performance significantly improves from the MEA using PP-BTMA bonded Pt/C, PP-BTMA bonded PtRu/C, to the MEA using PPA-HTMA bonded PtRu/C, and FLN bonded PtRu/C. This result suggests that the phenyl adsorption is one of the critical factors limiting the AEMFC performance.

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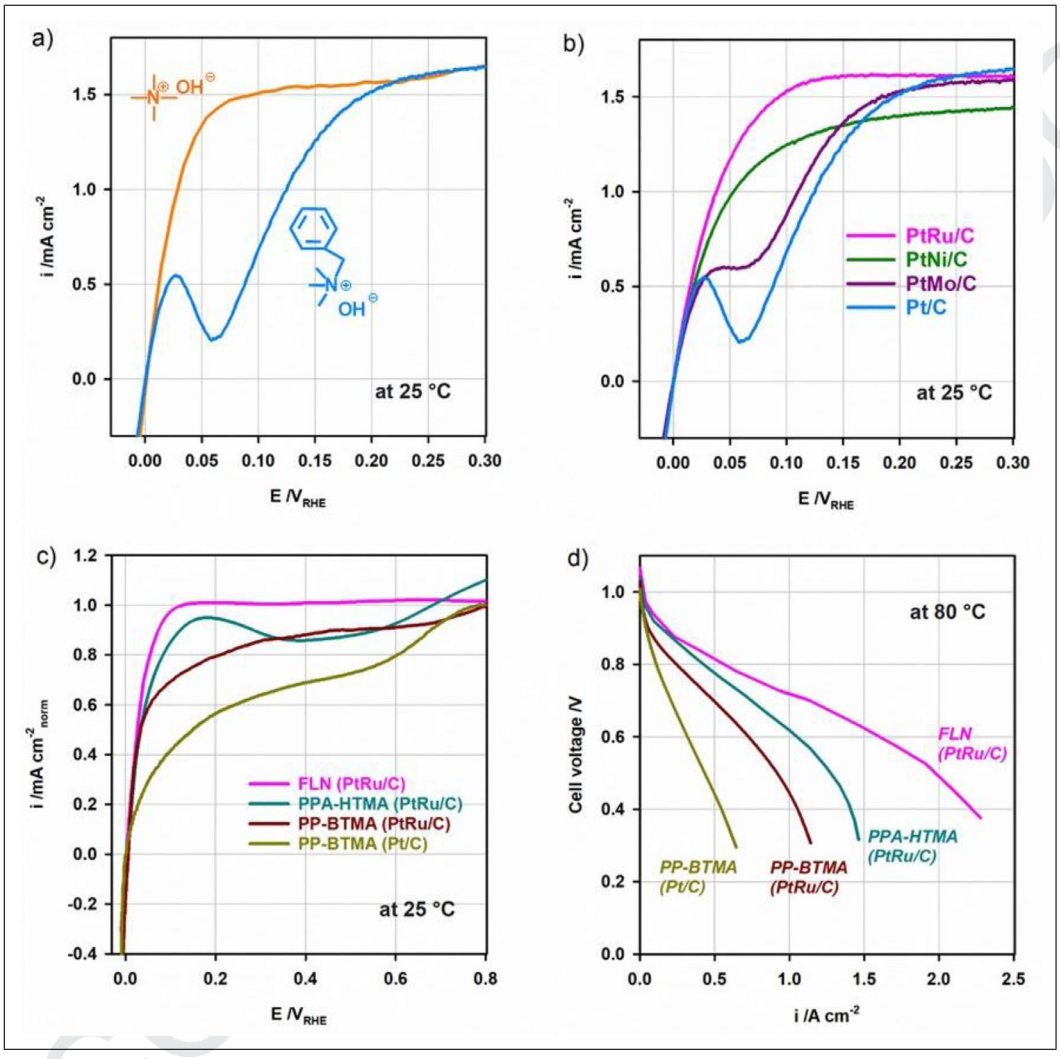
Figure 3



HOR voltammograms of (a) Pt/C in 0.1 M TMAOH and BTMAOH and (b) Pt alloy/C catalysts in 0.1 M BTMAOH. The voltammograms were measured from RDE at 25°C, rotating speed: 900 rpm, scan rate: 5 mV s^{-1}. Adapted with permission from *J. Phys. Chem. Lett.* 8, 4918-4924 (2017). Copyright © 2017 American Chemical Society. (c) HOR voltammogram of HOR catalyst in contact with ionomer. PP-BTMA: benzyltrimethyl ammonium functionalized poly(phenylene), PPA-HTMA: benzyltrimethyl ammonium functionalized poly(alkyl phenylene). FLN: poly(fluorene). The voltammograms were measured by microelectrode half-cell at 25°C (d) AEMFC performance comparison of MEAs using the catalyst and ionomers used in the microelectrode half-cell. The performance was measured at 80°C at 287 kPa backpressure; anode flow rate: 500 sccm, cathode flow rate: 300 sccm. AEM (thickness): quaternized poly(terphenylene) (35 μm), anode catalyst (loading): Pt/C (0.6 mg_{metal} cm^{-2}) or PtRu/C (0.75 mg_{metal} cm^{-2}) cathode catalyst (loading): Pt/C (0.6 mg_{metal} cm^{-2}). Adapted with permission from *Chem. Mater.* 30, 2188-2192 (2018). Copyright © 2018 American Chemical Society.

Concluding remarks

The adsorption of ionomer on HOR catalysts plays a critical role in the AEMFC performance. Cation-hydroxide-water co-adsorption on HOR catalysts limits H_2 diffusion to the catalyst surface. The most effective mitigation strategy for the cation-hydroxide-water co-adsorption is to increase anode flow rate, but this is not a practical approach for AEMFCs. Phenyl adsorption on HOR catalysts, on the other hand, blocks the catalyst active sites. Proper design of HOR catalysts and ionomers can minimize the undesirable phenyl adsorption. A better understanding at the interface of catalyst-ionomer is essential to improve the AEMFC performance and durability.

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Declarations of interest

None

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • Paper of special interest
- •• Paper of outstanding interest.

1. Gottesfeld S, Dekel DR, Page M, Bae C, Yan YS, Zelenay P, Kim YS: **Anion exchange membrane fuel cells: current status and remaining challenges**. *J Power Sources* 2018, **375**:170–184.

2. Fujimoto C, Kim DS, Hibbs M, Wrobleski D, Kim YS: **Backbone stability of quaternized polyaromatics for alkaline membrane fuel cells**. *J Membr Sci* 2012, **423**:438–449.

3. Lin BC, Qiu LH, Qiu B, Peng Y, Yan F: **A soluble and conductive polyfluorene ionomer with pendant imidazolium groups for alkaline fuel cell applications**. *Macromolecules* 2011, **44**:9642–9649.

4. Arges C, Zhang L: **Anion exchange membranes' evolution toward high hydroxide ion conductivity and alkaline resiliency**. *ACS Appl Energy Mater* 2018, **1**:2991–3012.

5. Choe YK, Fujimoto C, Lee KS, Dalton LT, Ayers K, Henson NJ, Kim YS: **Alkaline stability of benzyl trimethyl ammonium functionalized polyaromatics: A computational and experimental study**. *Chem Mater* 2014, **26**:5675–5682.

6. Merle G, Wessling M, Nijmeijer K: **Anion exchange membranes for alkaline fuel cells: a review**. *J Membr Sci* 2011, **377**:1–35.

7. Sheng WC, Gasteiger HA, Shao-Horn Y: **Hydrogen oxidation and evolution reaction kinetics on platinum: acid vs alkaline electrolytes**. *J Electrochem Soc* 2010, **157** B1529-B1536.

8. Strmcnik D, Uchimura M, Wang C, Subbaraman R, Danilovic N, van der Vliet D, Paulikas AP, Stamenkovic VR, Markovic NM: **Improving the hydrogen oxidation reaction rate by promotion of hydroxyl adsorption**. *Nat Chem* 2013, **5**:300–306.

9. Durst J, Siebel A, Simon C, Hasche F, Herranz J, Gasteiger HA: **New insights into the electrochemical hydrogen oxidation and evolution reaction mechanism**. *Energy Environ Sci* 2014, **7**:2255–2260.

10. Sheng WC, Zhuang ZB, Gao MR, Zheng J, Chen JGG, Yan YS: **Correlating hydrogen oxidation and evolution activity on platinum at different pH with measured hydrogen binding energy**. *Nat Commun* 2015, **6**.

11. Li JK, Ghoshal S, Bates MK, Miller TE, Davies V, Stavitski E, Attenkofer K, Mukerjee S, Ma ZF, Jia QY: **Experimental proof of the bifunctional mechanism for the hydrogen oxidation in alkaline media**. *Angew Chem Int Edit* 2017, **56**:15594–15598.

12. • Davydova E, Mukerjee S, Frédéric J, Dekel DR: **Electrocatalysts for hydrogen oxidation reaction in alkaline medium–a review**. *ACS Catal* 2018, **8**:6665–6690.
This review article outlined the current understanding of platinum-group metal and platnum-group metal-free catalysts for alkaline HOR and directed to the possible directions for future investigations including catalyst-ionomer interfacial study.

13. Wang Y, Wang GW, Li GW, Huang B, Pan J, Liu Q, Han JJ, Xiao L, Lu JT, Zhuang L: **Pt-ru catalyzed hydrogen oxidation in alkaline media: oxophilic effect or electronic effect?** *Energy Environ Sci* 2015, **8**:177–181.

14. Wang L, Maqliocca E, Cunningham EL, Mustain WE, Poynton SD, Escudero-Cid R, Nasef MM, Ponce-Gonzalez J, Bance-Souahli R, Slade RCT, Whelligan DK, Varcoe JR: **An optimized synthesis of high performance radiation-grafted anion-exchange membranes**. *Green Chem* 2017.

15. Wang LQ, Brink JJ, Liu Y, Herring AM, Ponce-Gonzalez J, Whelligan DK, Varcoe JR: **Non-fluorinated pre-irradiation-grafted (peroxidated) LDPE-based anion-exchange membranes with high performance and stability**. *Energy Environ Sci* 2017, **10**:2154–2167.

16. • Omasta TJ, Park AM, Lamanna JM, Zhang Y, Peng X, Wang L, Jacobson DL, Varcoe JR, Hussey DS, Pivovar B, Mustain WE: **Beyond catalysis and membranes: visualizing and solving the challenge of electrode water accumulation and flooding in AEMFCs**. *Energy Environ Sci* 2018, **11**:551–558.
This is a most recent article that shows that the peak power density of an MEA using an polyolefinic ionomer (phenyl group-free polymer backbone) can reach 2W cm−2 under H2/O2 conditions.

17. Omasta TJ, Wang L, Peng X, Lewis CA, Varcoe JR, Mustain WE: **Importance of balancing membrane and electrode water in anion exchange membrane fuel cells**. *J Power Sources* 2018, **375**:205–213.

18. Lee KH, Cho DH, Kim YM, Moon SJ, Seong JG, Shin DW, Sohn JY, Kim JF, Lee YM: **Highly conductive and durable poly(arylene ether sulfone) anion exchange membrane with end-group cross-linking**. *Energy Environ Sci* 2017, **10**:275–285.

19. Zhu L, Zimudzi TJ, Wang Y, Yu XD, Pan J, Han JJ, Kushner DI, Zhuang L, Hickner MA: **Mechanically robust anion exchange membranes via long hydrophilic cross-linkers**. *Macromolecules* 2017, **50**:2329–2337.

20. Liu WC, Liu L, Liao JY, Wang LH, Li NW: **Self-crosslinking of comb-shaped polystyrene anion exchange membranes for alkaline fuel cell application**. *J Membr Sci* 2017, **536**: 133–140.

21. Hu C, Zhang QG, Lin CX, Lin Z, Li L, Soyekwo F, Zhu AM, Liu QL: **Multi-cation crosslinked anion exchange membranes from microporous troger's base copolymers**. *J Mater Chem A* 2018, **6**:13302–13311.

22. Zhu YA, He YB, Ge XL, Liang X, Shehzad MA, Hu M, Liu YZ, Wu L, Xu TW: **A benzyltetramethylimidazolium-based membrane with exceptional alkaline stability in fuel cells: role of its structure in alkaline stability**. *J Mater Chem A* 2018, **6**:527–534.

23. Mustain W.E., Catalysts, membranes, CO2 and water: requirements and pathways for high performing AEMFCs. Proceedings of the Workshop on Ion Exchange Membranes for Energy Applications - EMEA 2018, Bad Zwischenahn, June 26 - 28 2018.

24. Jervis R, Mansor N, Sobrido AJ, Jones S, Gibbs C, Neville TP, Millichamp J, Shearing PR, Brett DJL: **The importance of using alkaline ionomer binders for screening electrocatalysts in alkaline electrolyte**. *J Electrochem Soc* 2017, **164** F1551-F1555.

25. Artyushkova K, Workman MJ, Matanovic I, Dzara MJ, Ngo C, Pylypenko S, Serov A, Atanassov P: **Role of surface chemistry on catalyst/ionomer interactions for transition metal-nitrogen-carbon electrocatalysts**. *ACS Appl Energy Mater* 2018, **1**:68–77.

26. Sabbe MK, Laín L, Reyniers M-F, Marin GB: **Benzene adsorption on binary Pt_3M alloys and surface alloys: a DFT study**. *Phys Chem Chem Phys* 2013, **15**:12197–12214.

27. • Unlu M, Abbott D, Ramaswamy N, Ren XM, Mukerjee S, Kohl PA: **Analysis of double layer and adsorption effects at the alkaline polymer electrolyte-electrode interface**. *J Electrochem Soc* 2011, **158**:B1423–B1431.
The authors in this work first observed the cummulative cation adsorption on Pt electrode in 0.1M TMAOH. This study also showed the potential dependency of the cation degradation and methanol oxidation inhibition by the cation adsorption.

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28. McCrum IT, Janik MJ: **PH and alkali cation effects on the Pt cyclic voltammogram explained using density functional theory**. *J Phys Chem C* 2016, **120**:457–471.
•• The DFT study is of outstanding interest as it described the involvement of hydroxide and water co-adsorbates in addition to potassium cation on the cyclic voltammogram under high pH conditions. This paper also explains the peak shifts of Pt(111), Pt(100) and Pt(110) facets in the cyclic voltammograms.

29. McCrum IT, Hickner MA, Janik MJ: **Quaternary ammonium cation specific adsorption on platinum electrodes: a combined experimental and density functional theory study**. *J Elctrochem Soc* 2018, **165**:F114–F121.

30. Chung HT, Martinez U, Chlistunoff J, Matanovic I, Kim YS: **Cation-hydroxide-water co-adsorption inhibits the alkaline hydrogen oxidation reaction**. *J Phys Chem Lett* 2016, **7**:4464–4469.
•• This paper reveals the inthibition mechanism of cation-hydroxide-water co-adsorption using an impedance study. The impact of co-adsorption on HOR voltammogram is also addressed in terms of RDE potentials and chronoamperometry.

31. Dunwell M, Wang JH, Yan Y, Xu B: **Surface enhanced spectroscopic investigations of adsorption of cations on electrochemical interfaces**. *Phys Chem Chem Phys* 2017, **19**:971–975.

32. Yim SD, Chung HT, Chlistunoff J, Kim DS, Fujimoto C, Yang TH, Kim YS: **A microelectrode study of interfacial reactions at the platinum-alkaline polymer interface**. *J Electrochem Soc* 2015, **162**:F499–F506.

33. Dumont J.H., Hjelm R., Watkins E.B., Chung H.T., Martinez U., Atanassov P., Kim Y.S., Investigating catalyst-electrolyte interface by microelectrode, infrared reflection adsorption spectroscopy and neutron reflectometry. Proceedings of the 230th ECS meeting, PRiME 2016, Honolulu, Hawaii, October 2-7 2016.

34. Subbaraman R, Danilovic N, Lopes PP, Tripkovic D, Strmcnik D, Stamenkovic VR, Markovic NM: **Origin of anomalous activities for electrocatalysts in alkaline electrolytes**. *J Phys Chem C* 2012, **116**:22231–22237.
• This paper is of particular interest since the authors found that 3*d*-transition metal cations and the formation of hydroxides cause an anomalous activities of electrocatalysts in alkaline electrolytes.

35. Schouten KJP, van der Niet MJTC, Koper MTM: **Impedance spectroscopy of H and OH adsorption on stepped single-crystal platinum electrodes in alkaline and acidic media**. *Phys Chem Chem Phys* 2010, **12**:15217–15224.

36. Chen XT, McCrum IT, Schwarz KA, Janik MJ, Koper MTM: **Co-adsorption of cations as the cause of the apparent pH dependence of hydrogen adsorption on a stepped platinum single-crystal electrode**. *Angew Chem Int Edit* 2017, **56**:15025–15029.

37. Ruetschi P: **Solubility and diffusion of hydrogen in strong electrolytes and generation and consumption of hydrogen in sealed primary batteries**. *J Electrochem Soc* 1967, **114**:301–305.

38. Park EJ, Kim YS: **Quaternized aryl ether-free polyaromatics for alkaline membrane fuel cells: synthesis, properties, and performance–a topical review**. *J Mater Chem A* 2018, **6**:15456–15477.

39. Omasta TJ, Peng X, Miller HA, Vizza F, Wang L, Varcoe JR, Dekel DR, Mustain WE: **Beyond 1.0W cm^{-2} performance without platinum - the beginning of a new era in anion exchange membrane fuel cells**. *J Electrochem Soc* 2018:J3039–J3044.

40. Maurya S, Noh S, Matanovic I, Park EJ, Narvaez Villarrubia C, Han J, Bae C, Kim YS: **Rational design of polyaromatic ionomers for alkaline membrane fuel cells with >1W cm^{-2} power density**. *Energy & Environ Sci* 2018 Accepted.
• This paper showed a design strategy for anion exchange ionomers that involves minimizing phenyl adsorption on the catalyst. This paper also demonstrated a high AEMFC performance of an MEA employing quaternized poly(fluorene) ionomer and PtRu/C anode catalysts.

41. Pan J, Zhu L, Han JJ, Hickner MA: **Mechanically tough and chemically stable anion exchange membranes from rigid-flexible semi-interpenetrating networks**. *Chem Mater* 2015, **27**:6689–6698.

42. He YB, Ge XL, Liang X, Zhang JJ, Shehzad MA, Zhu Y, Yang ZJ, Wu L, Xu TW: **Anion exchange membranes with branched ionic clusters for fuel cells**. *J Mater Chem A* 2018, **6**:5993–5998.

43. Lin CX, Wu HY, Li L, Wang XQ, Zhang QG, Zhu AM, Liu QL: **Anion conductive triblock copolymer membranes with flexible multication side chain**. *ACS Appl Mater Inter* 2018, **10**:18327–18337.

44. Yang Q, Li L, Lin CX, Gao XL, Zhao CH, Zhang QG, Zhu AM, Liu QL: **Hyperbranched poly(arylene ether ketone) anion exchange membranes for fuel cells**. *J Membr Sci* 2018, **560**:77–86.

45. Maurya S, Dumont JH, Narvaez Villarrubia C, Matanovic I, Li D, Kim YS, Noh S, Han J, Bae C, Miller HA, Fujimoto C, Dekel DR: **Surface adsorption affects the performance of alkaline anion-exchange membrane fuel cells**. *ACS Catal* 2018. https://doi.org/10.1021/acscatal.8b03227.

46. Chung HT, Choe YK, Martinez U, Gonzalez I, Mohanti A, Bae C, Kim YS: **Effect of organic cations on hydrogen oxidation reaction of carbon supported platinum**. *J Electrochem Soc* 2016, **163**:F1503–F1509.

47. Lehwald S, Ibach H, Demuth JE: **Vibration spectroscopy of benzene adsorbed on Pt(111) and Ni(111)**. *Surf Sci* 1978, **78**:577–590.

48. Soriaga MP, Hubbard AT: **Determination of the orientation of adsorbed molecules at solid-liquid interfaces by thin-layer electrochemistry - aromatic-compounds at platinum-electrodes**. *J Am Chem Soc* 1982, **104**:2735–2742.

49. Hartung T, Schmiemann U, Kamphausen I, Baltruschat H: **Electrodesorption from single-crystal electrodes - analysis by differential electrochemical mass-spectrometry**. *Anal Chem* 1991, **63**:44–48.

50. Rodriguez JL, Pastor E: **A comparative study on the adsorption of benzyl alcohol, toluene and benzene on platinum**. *Electrochim Acta* 2000, **45**:4279–4289.

51. Montilla F, Morallon E, Vazquez JL: **Electrochemical study of benzene on pt of various surface structures in alkaline and acidic solutions**. *Electrochim Acta* 2002, **47**:4399–4406.

52. Reshetenko TV, St-Pierre J: **Study of the aromatic hydrocarbons poisoning of platinum cathodes on proton exchange membrane fuel cell spatial performance using a segmented cell system**. *J Power Sources* 2016, **333**:237–246.

53. Matanovic I, Chung HT, Kim YS: **Benzene adsorption: A significant inhibitor for the hydrogen oxidation reaction in alkaline conditions**. *J Phys Chem Lett* 2017, **8**:4918–4924.
•• This paper shows the impact of phenyl adsorption on alkaline HOR voltammograms by comparing HOR voltammograms of Pt in 0.1M TMAOH and BTMAOH. The effect of alloying Pt with other metals such as Mo, Ni, and Ru is explained based on DFT calculations and RDE experiments.

54. Morin C, Simon D, Sautet P: **Trends in the chemisorption of aromatic molecules on a Pt(111) surface: benzene, naphthalene, and anthracene from first principles calculations**. *J Phys Chem B* 2004, **108**:12084–12091.

55. Peng HG, Li QH, Hu MX, Xiao L, Lu JT, Zhuang L: **Alkaline polymer electrolyte fuel cells stably working at 80 degrees C**. *J Power Sources* 2018, **390**:165–167.

56. Maurya S, Fujimoto C, Hibbs MR, Narvaez Villarrubia C, Kim YS: **Toward improved alkaline membrane fuel cell performance using quaternized aryl ether-free polyaromatics**. *Chem Mater* 2018, **30**:2188–2192.

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