2019 Anion Exchange Membrane Workshop
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Catalyst-ionomer Interactions/AMFC Durability

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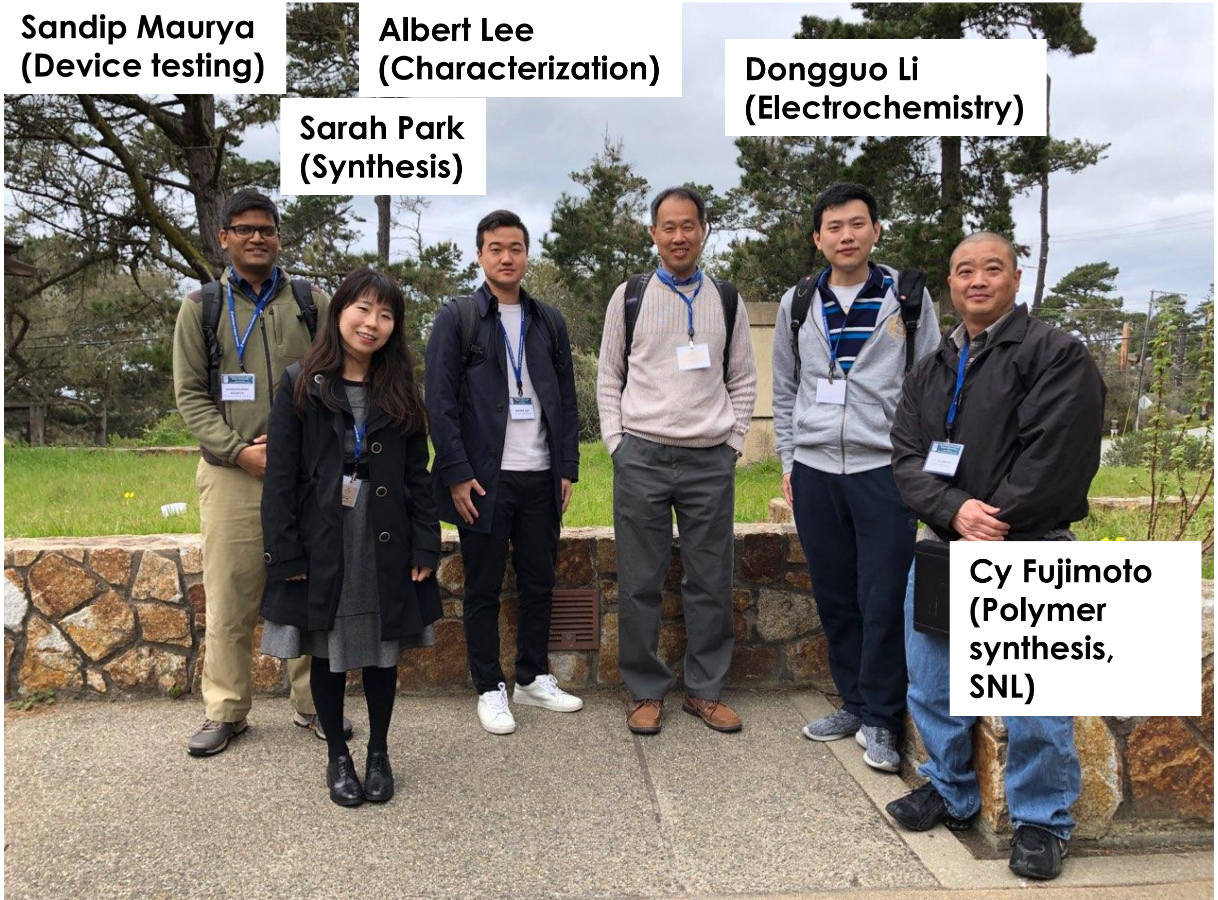
Acknowledgment



Sandip Maurya (Device testing)

Albert Lee (Characterization)

Sarah Park (Synthesis)

Dongguo Li (Electrochemistry)

Cy Fujimoto (Polymer synthesis, SNL)

Collaborators

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Joseph Dumont (LANL)
Rex Hjelm (former LANL)

NIST neutron center
LANSCE neutron center

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DOE EERE FCTO

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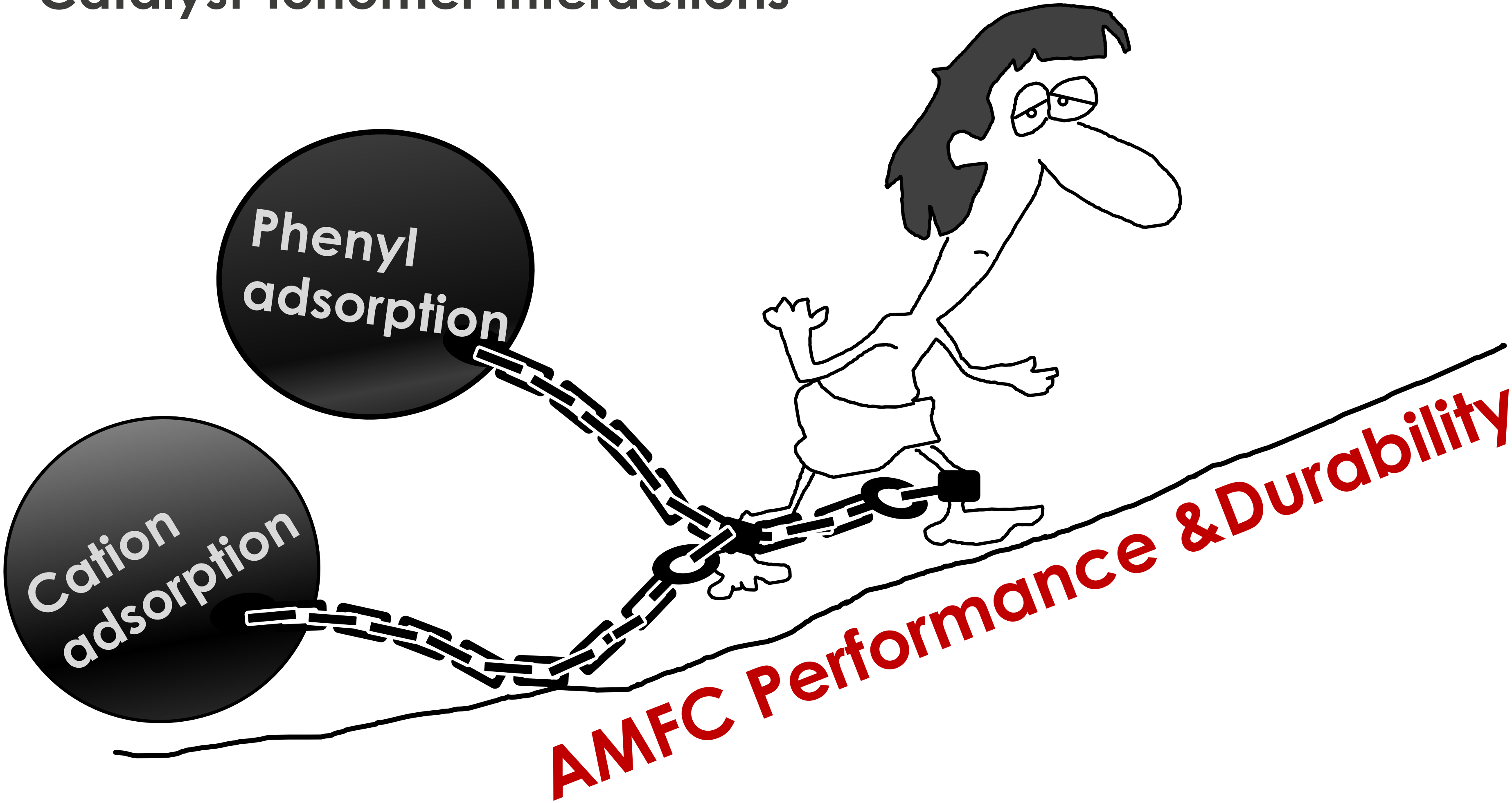
Research Focus	Major Founding
AEM **Stability** **(2016)**	**Polymer backbone degradation[1]**
AEMFC **Performance** **(2017-2019)**	**Phenyl group adsorption[2]** **Cation-hydroxide-water co-adsorption[3]**
AEMFC **Durability** **(2019)**	**Oxidation of phenyl group (in the cathode ionomer)** **Degradation of ammonium group (in the anode ionomer)**

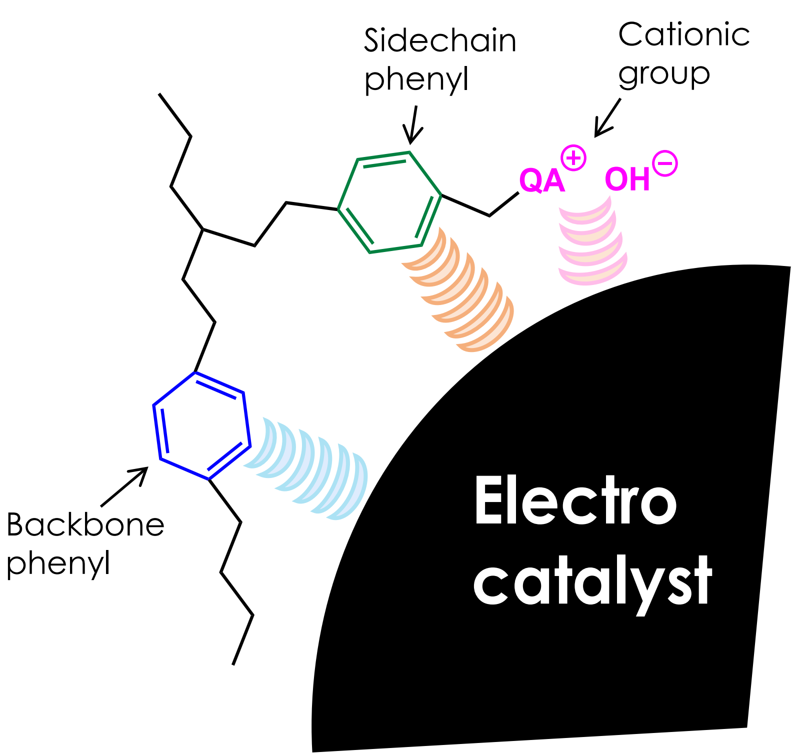
[1]Fujimoto et al. *J. Memb. Sci.* 423-424, 438-449, 2012; [2]Matanovic et al. *J. Phy. Chem. Let.* 8, 4918-4924, 2017; [3]Li et al. *Cur. Opinion in Electrochem.*, 12, 189-195, 2018; [4]S. Murya, S. *Energy & Environ. Sci.* 11, 3283-3291, 2019

Catalyst-Ionomer Interactions

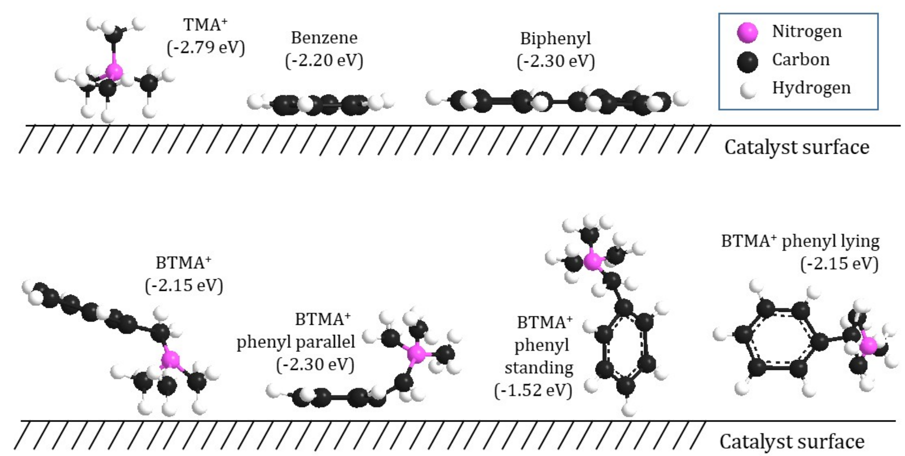


Adsorption of ionomer fragment on electrocatalysts

Anion exchange ionomer



Adsorption energy calculated by DFT

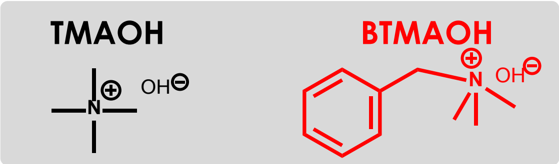


Those adsorptions are unique phenomena for alkaline ionomer because acid system uses perfluorosulfonic acid.

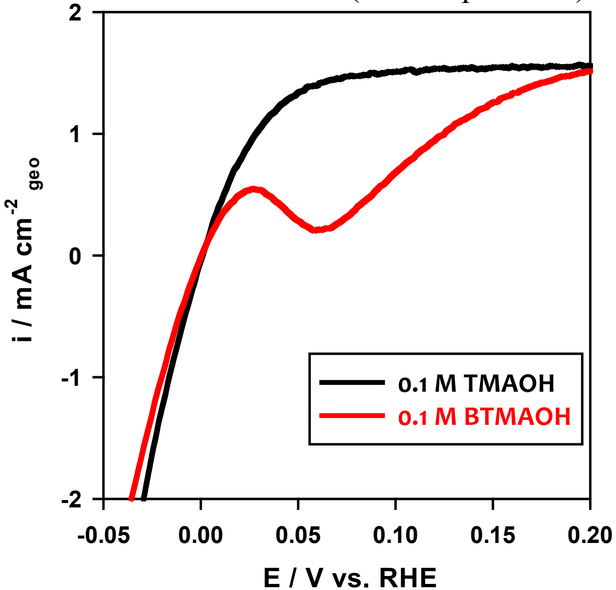
Li et al. Curr. Opin. Electrochem. 12, 189-195 (2018)

Impact of phenyl adsorption on HOR catalyst on AMFC performance

Identification of phenyl group adsorption on Pt at HOR potential

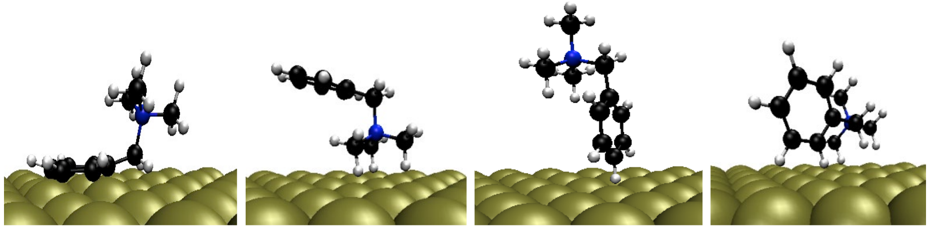


HOR voltammogram of Pt/C
(RDE experiment)



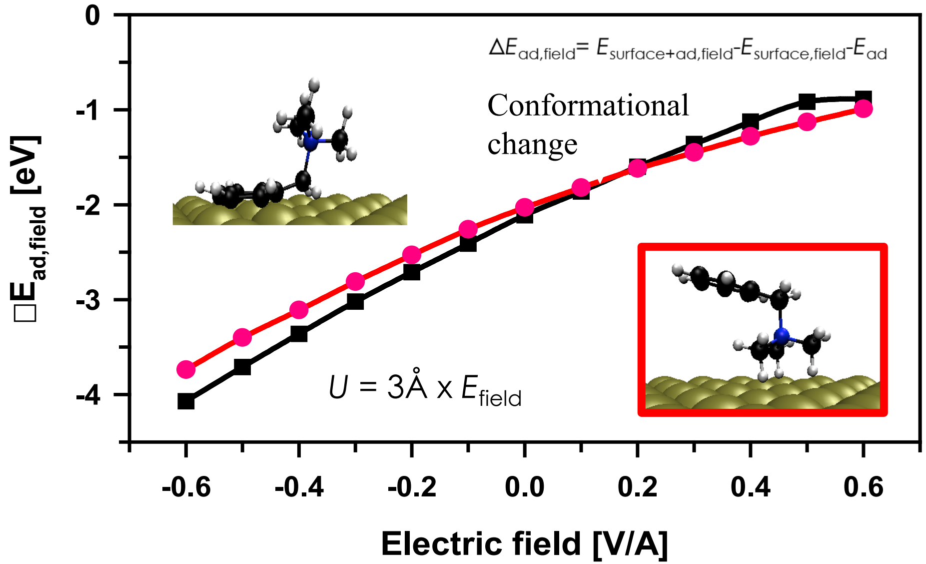
Matanovic et al. J. Phys. Chem. Lett. 8, 4918 (2017)

Adsorption Position (side view) of BTMA on Pt(111) at U = 0 V

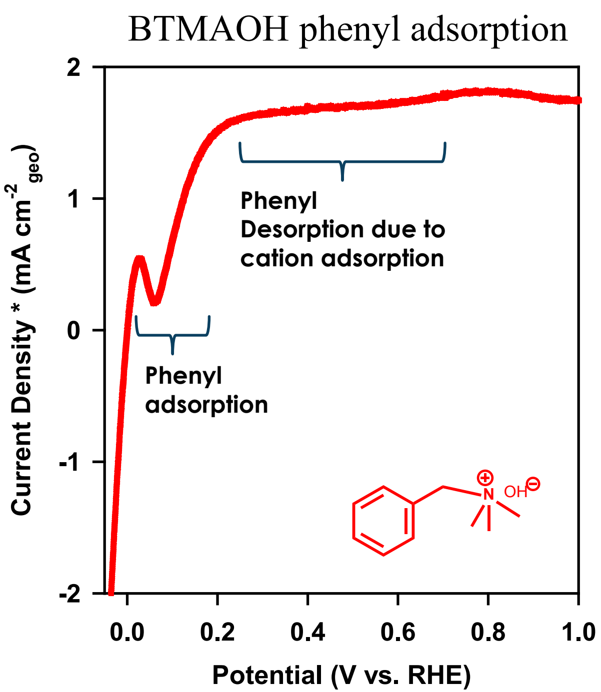


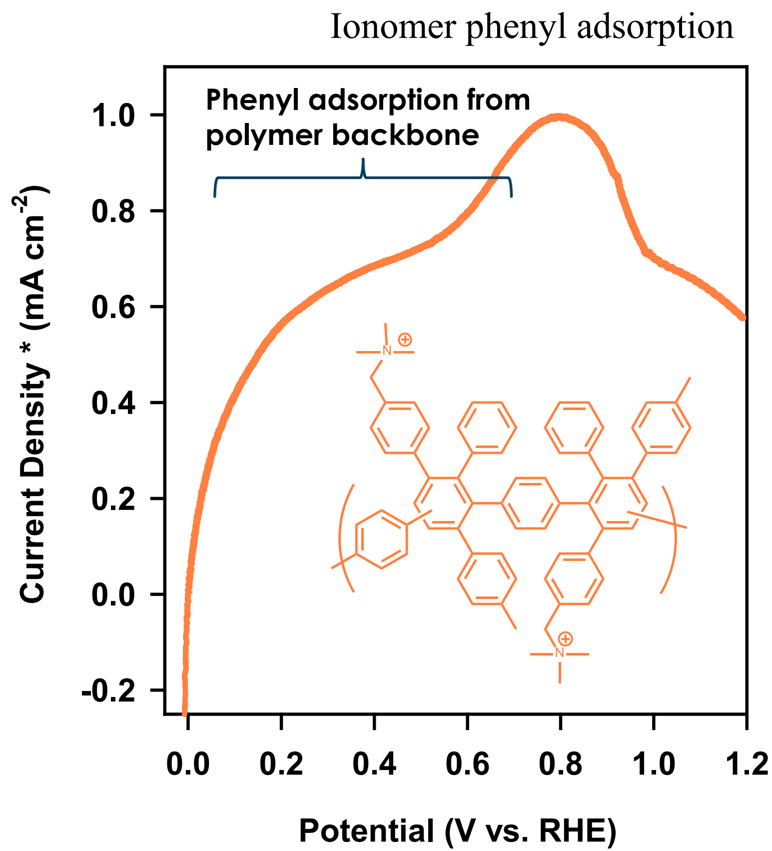
ΔE=-2.30 eV ΔE=-2.15 eV ΔE=-1.51 eV ΔE=-2.15 eV

Effect of Applied Potential on the Interaction



Impact of backbone phenyl adsorption on HOR of Pt



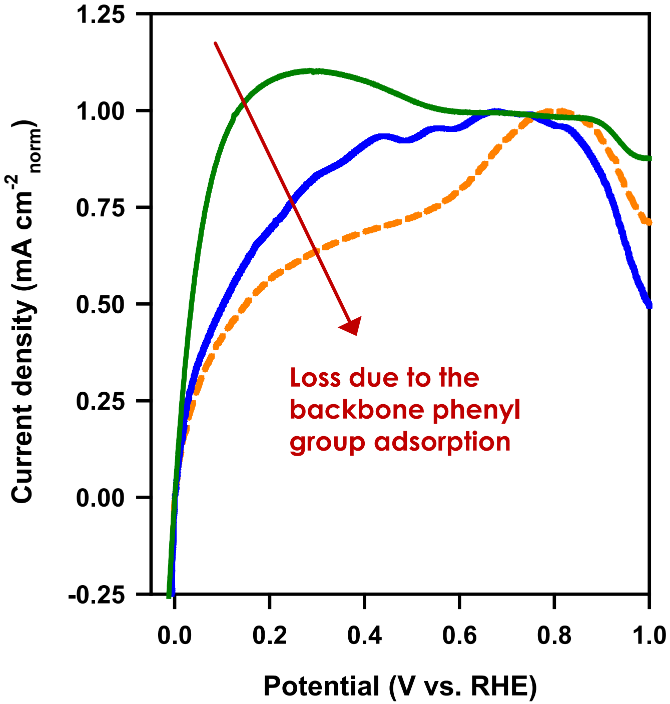


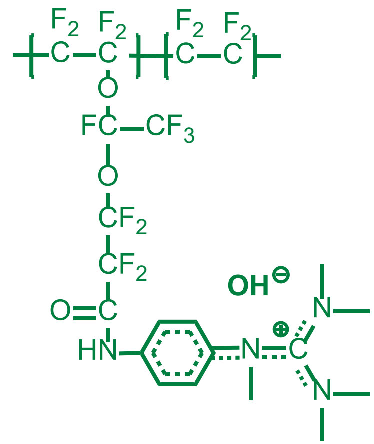
- Backbone phenyl impacts the HOR up to 0.8 V vs. RHE, more significant than ammonium functionalized phenyl group.

Maurya et al. Chem. Mater. 30, 2188 (2018)
Matanovic et al. J. Phys. Chem. Lett. 8, 4918 (2017)

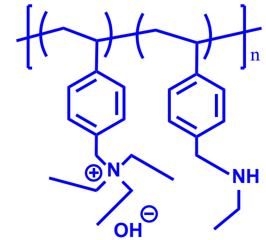
Impact of ionomer type on HOR of Pt

Pt microelectrode in contact with quaternized polymers

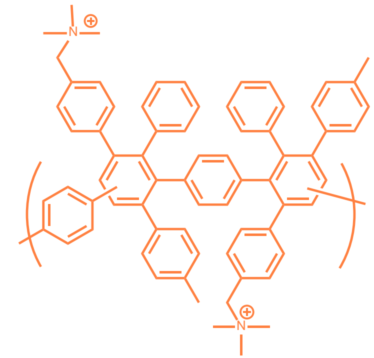




Perfluorinated (2013 LANL)



Polyolefinic (2018 LANL)



Poly(phenylene) (2012 SNL)

- As the number of ammonium unsubstituted phenyl group increased, the HOR activity decreases.

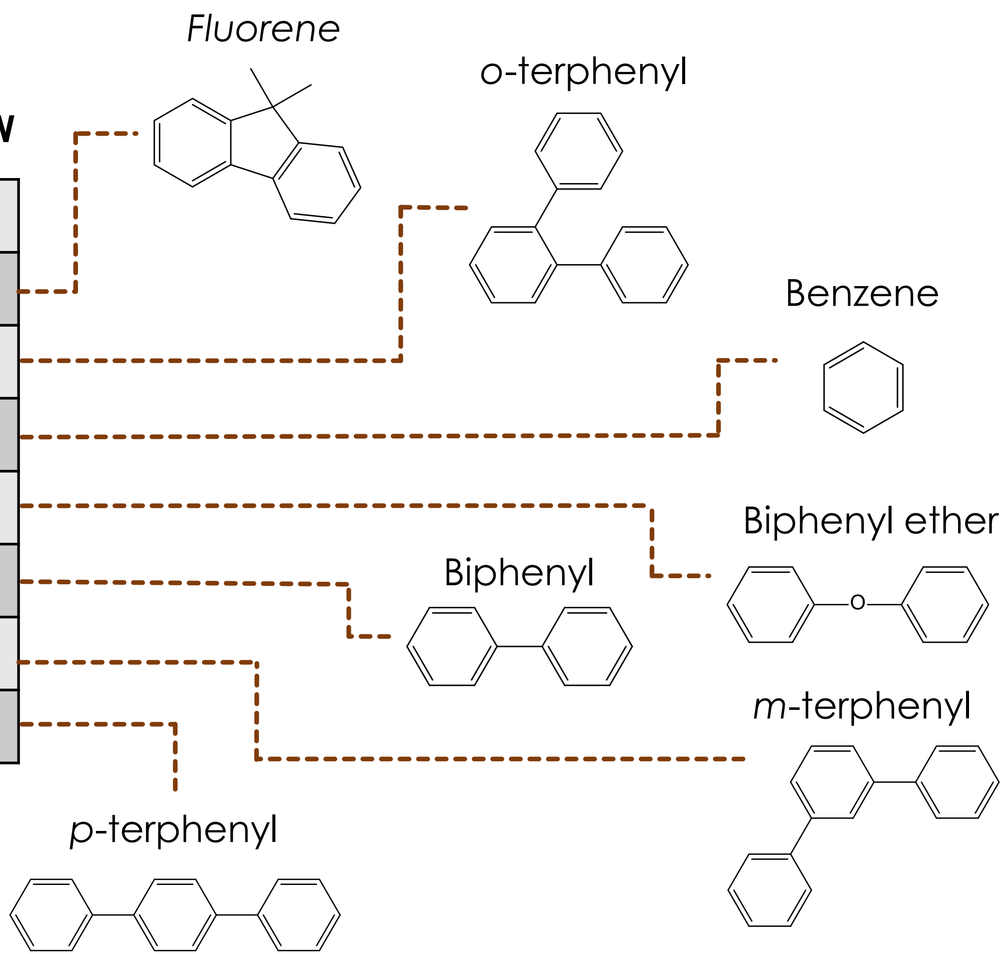
Maurya et al. Chem. Mater. 30, 2188 (2018)

The adsorption energy of polymer backbone phenyl fragment on Pt(111) by DFT calculation

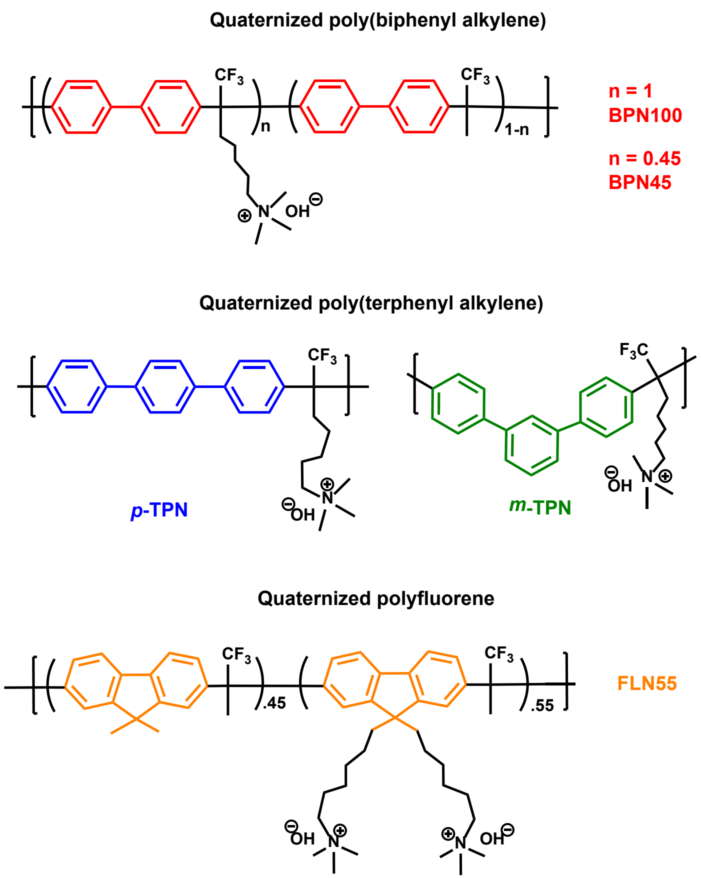
Adsorption energies (in eV) using optPBE-vdW

Fragment	E_{ad} (eV)	rank
fluorene	-1.38	1
o-terphenyl	-1.52	2
benzene*	-1.95	3
biphenyl ether	-2.19	4
biphenyl	-2.87	5
m-terphenyl	-3.61	6
p-terphenyl	-3.94	7

Matanovic et al. Chem. Mater. in press (2019)

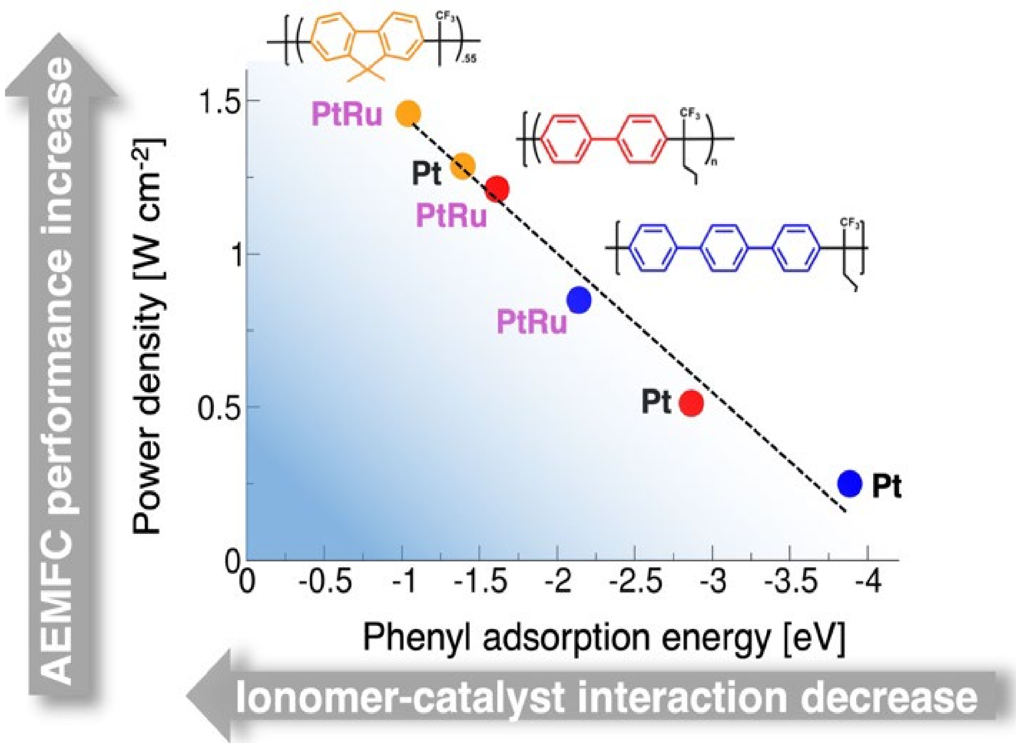


Impact of phenyl group adsorption on AMFC performance



Courtesy: Prof. Bae at RPI

AMFC performance of MEAs using different ionomers

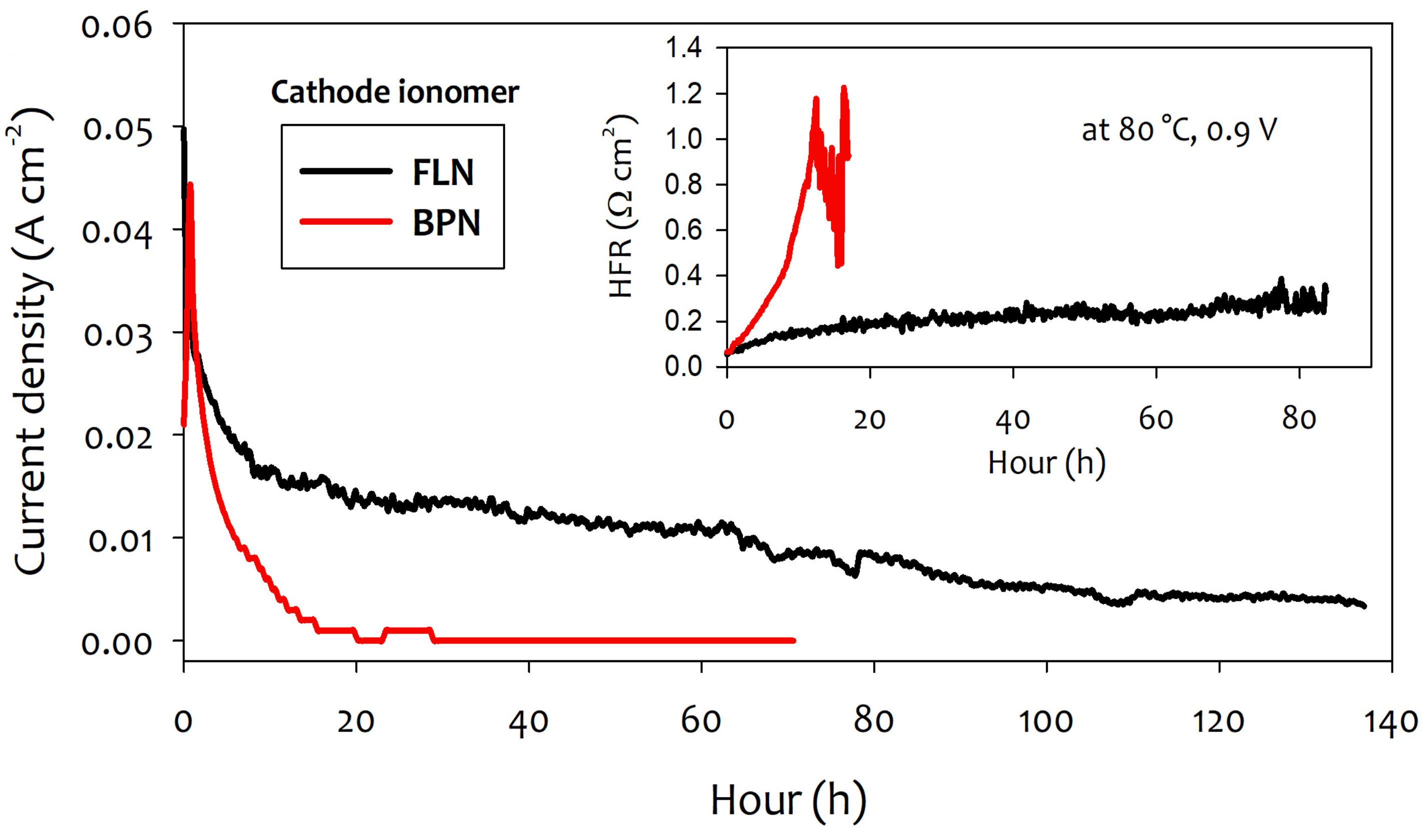


Matanovic et al. Chem. Mater. in press (2019)

Impact of phenyl adsorption on ORR and OER catalysts on AMFC and AEM electrolyzer durability

Discovery of the impact of phenyl adsorption on ORR or OER durability

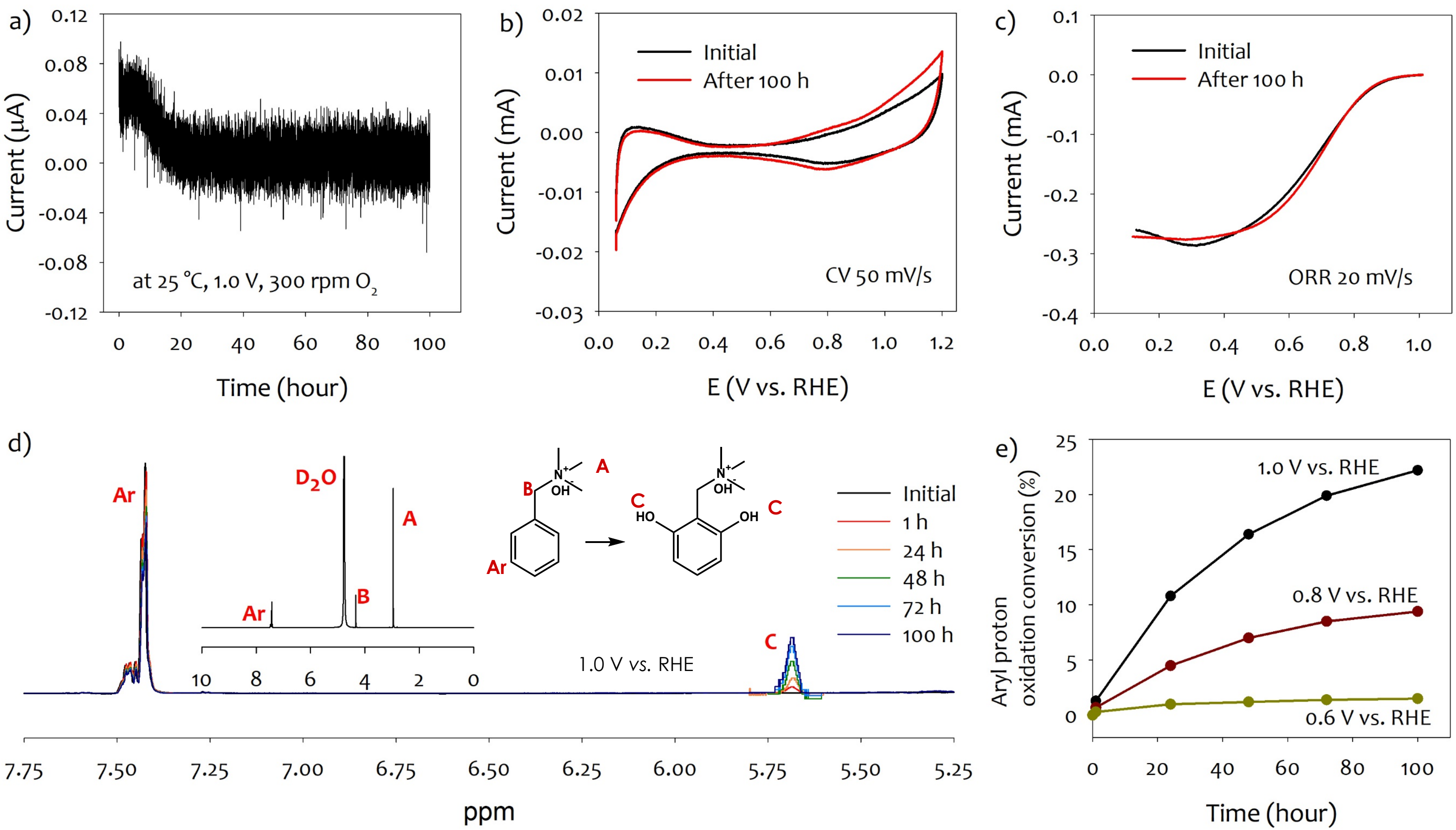
AMFC current density change of two MEAs (only cathode ionomer is different)



- An MEA using less phenyl adsorbing ionomer (FLN) showed better AMFC durability

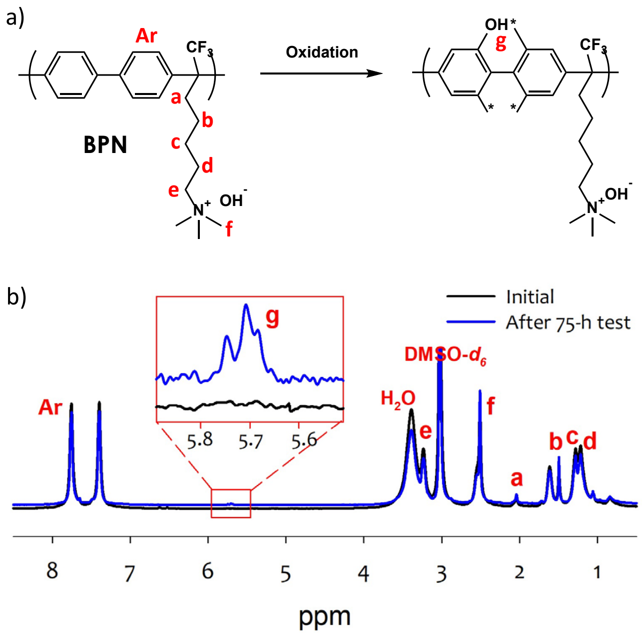
Identification of phenyl group adsorption on Pt at ORR potential

ORR current changes, CV, ORR voltammograms and ^1H NMR analysis of BTMAOH

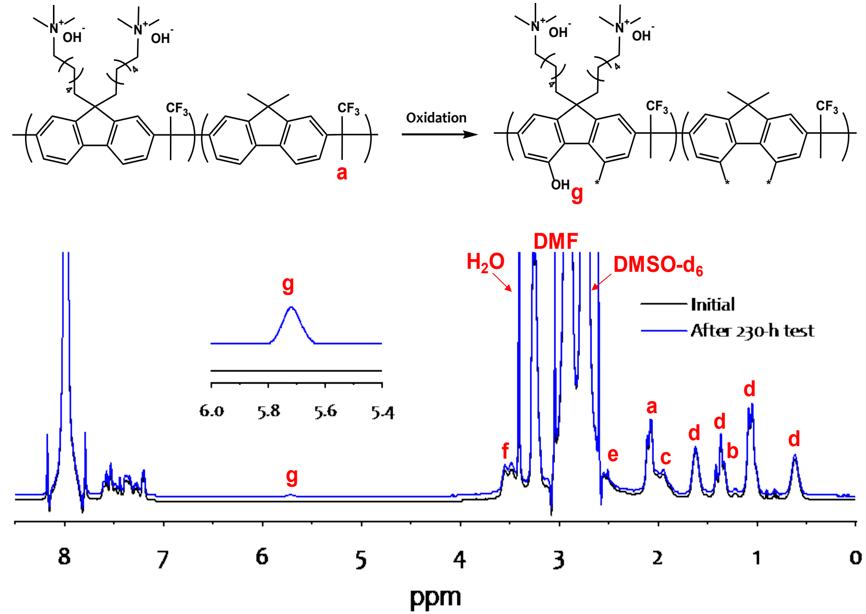


Detection of the phenol group formation from cathode ionomer

[1]H NMR analysis of cathode ionomer (BPN) after 75 hours of AMFC operation at 0.9 V



[1]H NMR analysis of cathode ionomer (FLN) after 230 h hours of AMFC operation at 0.9 V

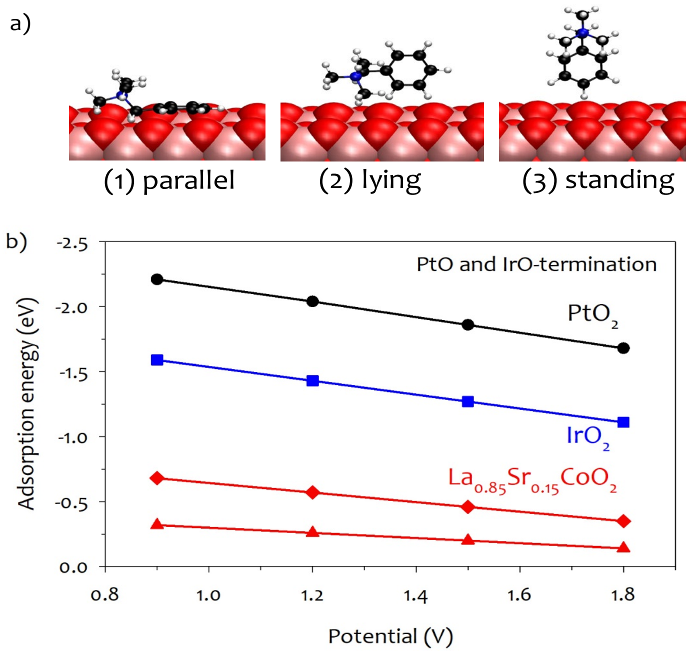


- Phenyl oxidation for BPN: 1.3% after 75 h vs. 0.34% after 230 h

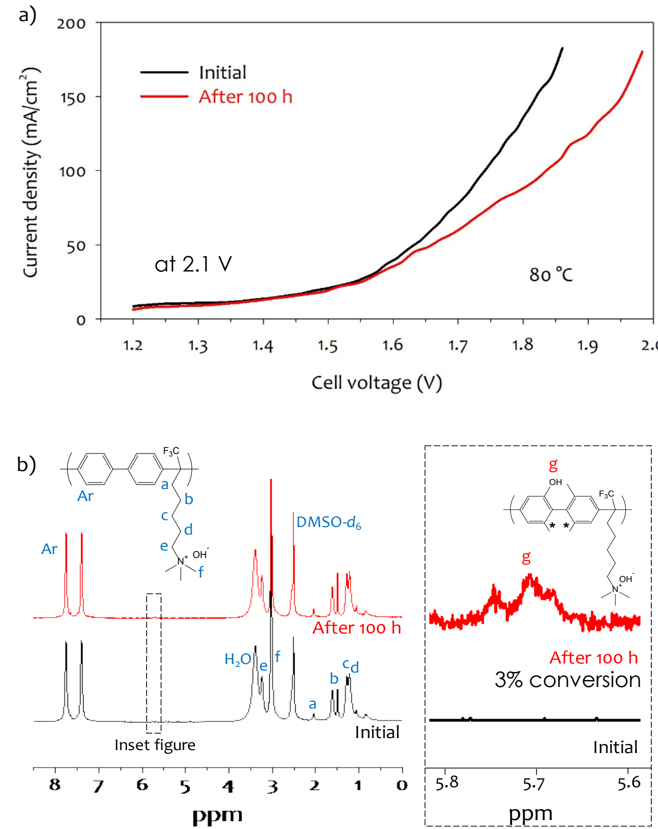
Maurya et al. Manuscript under review, J. Power Sources (2019)

Phenyl oxidation at OER potential (AEM electrolysis)

Phenyl adsorption energy (DFT calculation)



iV curves of IrO_2 catalyzed AEM electrolyzer

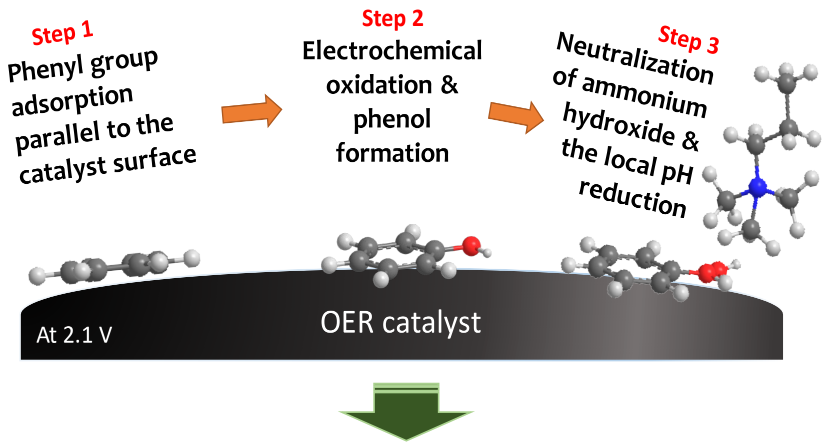


- PGM catalysts have high phenyl adsorption energy and the AEM electrolyzer using the OER catalysts showed performance decay.

Li et al. ACS Appl. Mater. Interf. 11, 9696-9701 (2019)

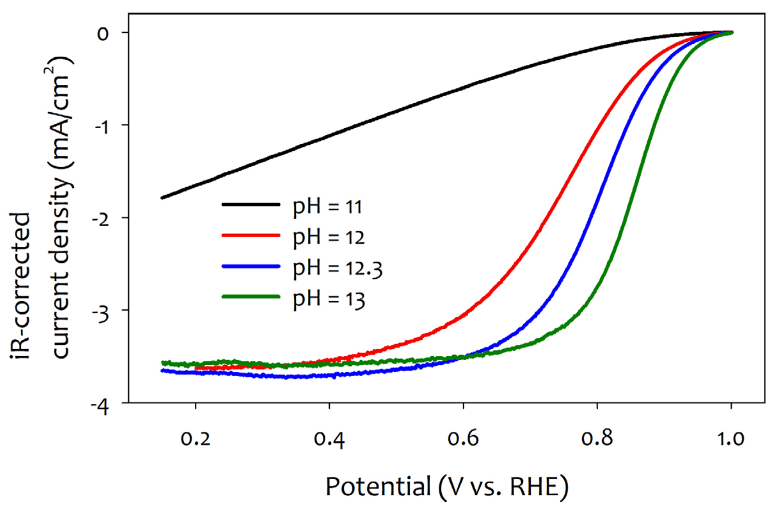
Take-home message for phenyl oxidation

Degradation mechanism



Performance decay of AEM electrolyzer over time

Effect of pH on Pt ORR activity

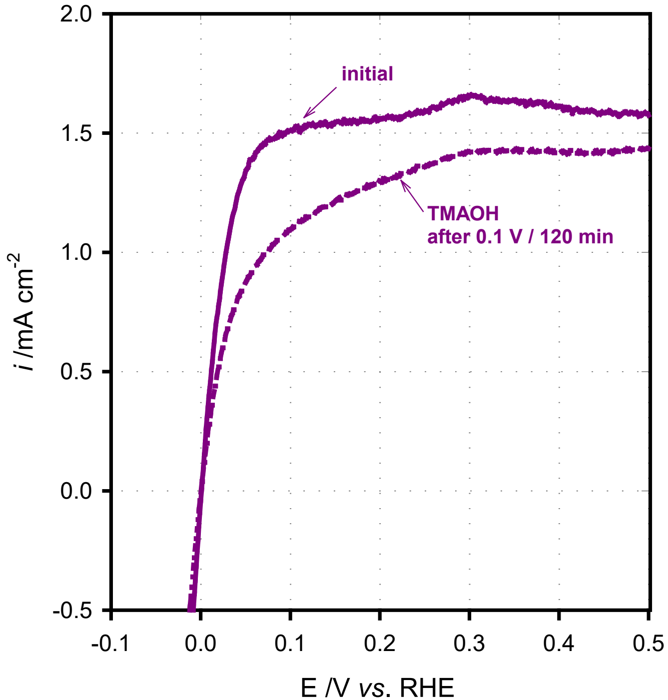


- The concentration of phenol at the catalyst-ionomer interface is much higher than that in the bulk ionomer.
- The impact is similar to carbonation but this brings permanent damage to the cell → more significant than carbonation.

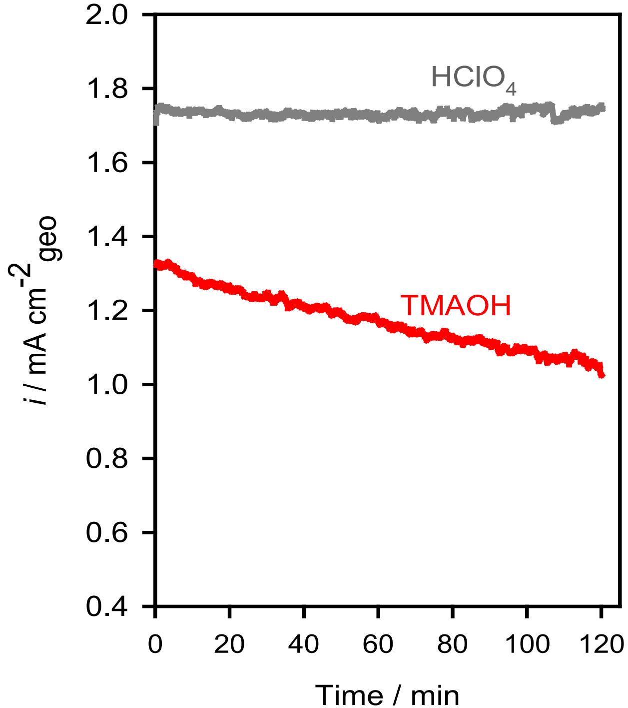
Impact of cation adsorption on HOR catalysts on AMFC performance

Identification of cation adsorption on Pt at HOR potential

HOR voltammogram of Pt/C in 0.1 M TMAOH



Chronoamperometry at 0.1 V *vs.* RHE

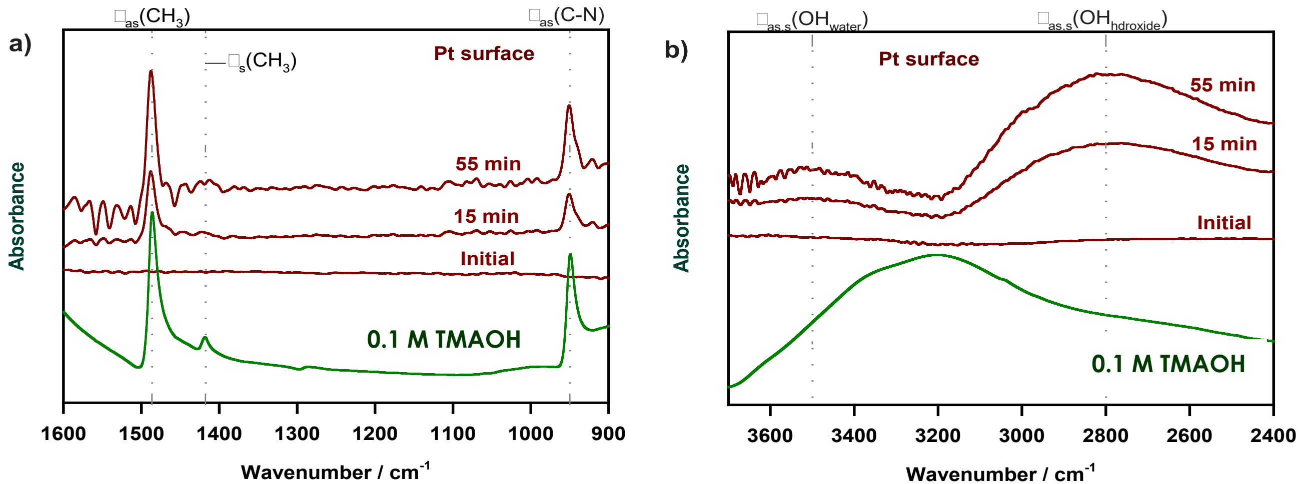


- HOR activity of Pt in TMAOH decreases after exposure the electrode at 0.1 V vs. RHE

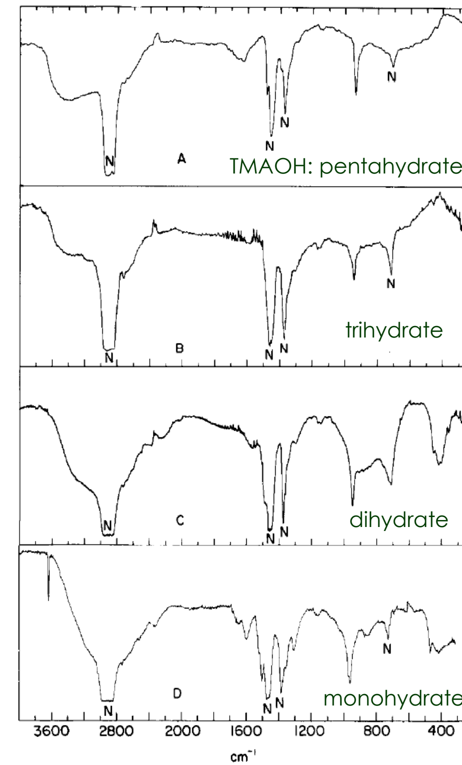
Chung et al. J. Electrochem. Soc. 163, F1503-F1509 (2019)

Detection of TMA-water co-adsorption on Pt at 0.1 V vs. RHE

IRRAS in the (a) fingerprint and (b) O-H stretching regions during chronoamperometry of Pt in 0.1 M TMAOH



FTIR of highly conc. TMAOH



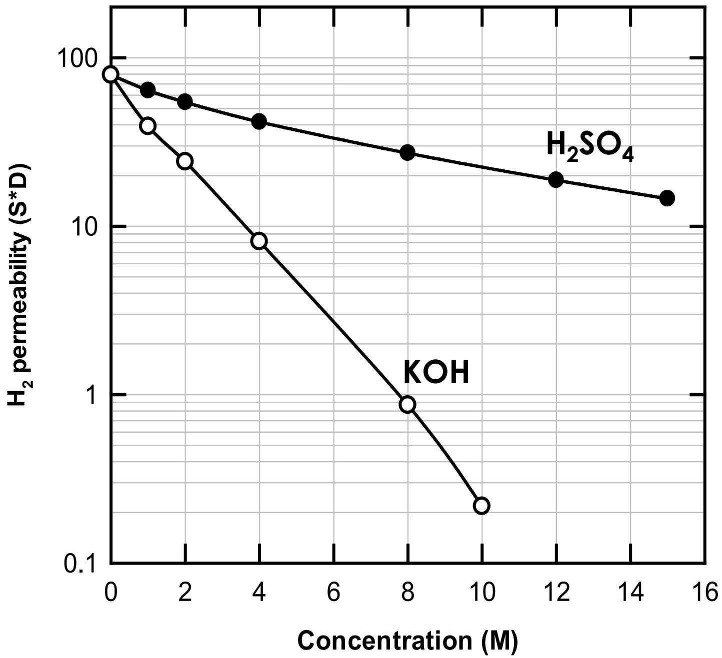
- Time-dependent cation adsorption on Pt at 0.1 V vs. RHE.
- OH stretching region indicates that the co-adsorbed layer has high concentration of cationic group vs. water.

Harmon et al. J. Mol. Struc. 159, 255-263 (1987)

Chung et al. J. Phys. Chem. Lett. 7, 4464-4469 (2016)

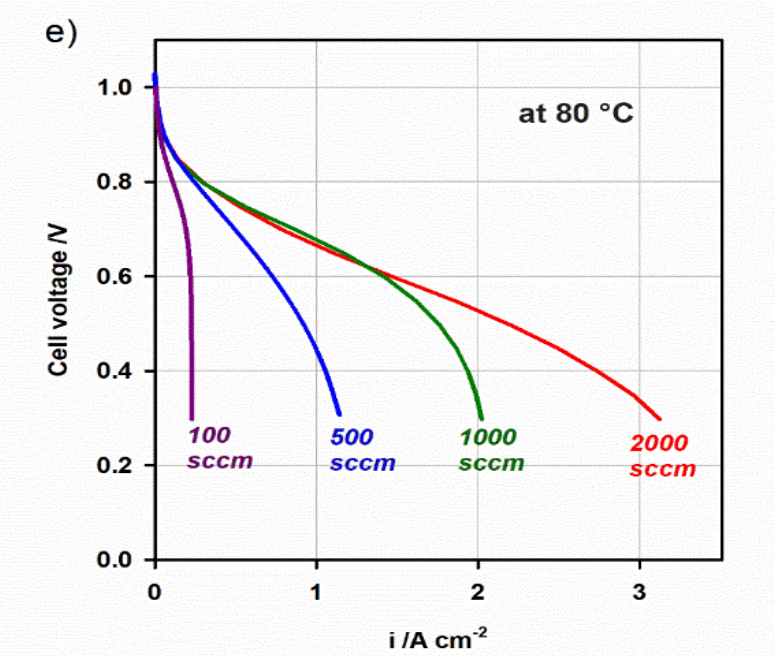
Impact of co-adsorption on hydrogen diffusion

H_2 permeability in H_2SO_4 and KOH as a function of the concentration.



Ruetschi J. Electrochem. Soc.114, 301 (1967)

Impact of anode flow rate on AMFC performance



AEM (thickness): quaternized poly(terphenylene) (35 μm), ionomer: BPN, anode catalyst: PtRu/C (0.75 mg_{metal} cm^{-2}) cathode catalyst: Pt/C (0.6 mg_{metal} cm^{-2}), cathode flow rate: 300 sccm of O_2.

Li et al. Curr. Opin. Electrochem. 12, 189-195 (2018)

Anode ionomer design aspect towards highly-performing AMFCs

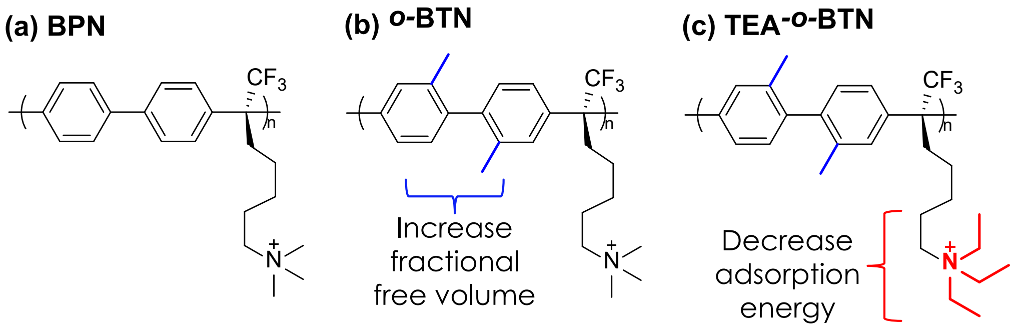
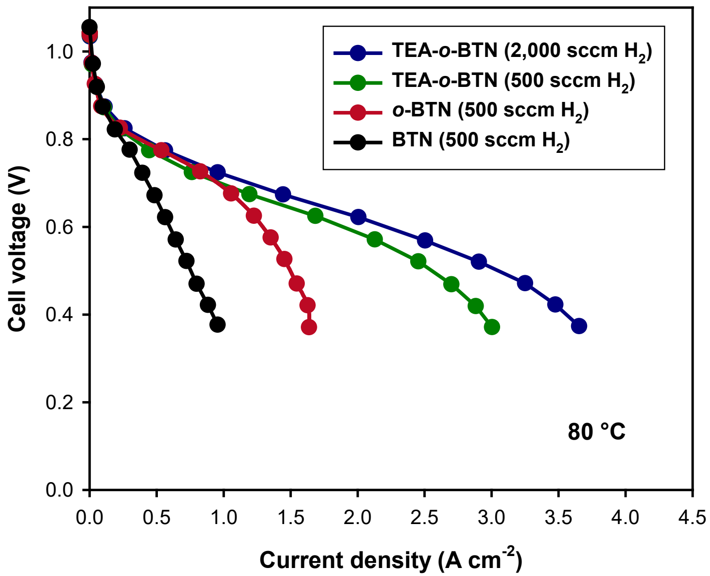


Table. Self-diffusion coefficients of H_2 in BPN and o-BTN dispersions by PFG ^{1}H NMR

Temperature (°C)	Diffusion coefficient / (10^{-9} m^2 s^{-1})		
	BPN	o-BPN	Fold increase
25	2.69	8.00	3.0
40	3.24	12.45	3.8
65	3.78	17.58	4.7
80	4.45	22.30	5.0

Impact of anode ionomer structure on AMFC performance



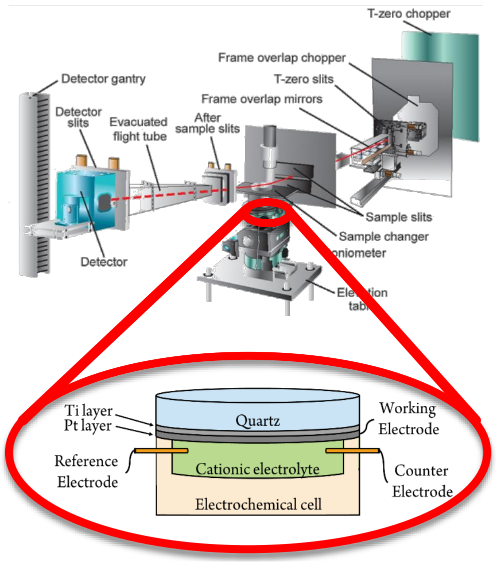
- Impact of the cationic group is more significant → Research need

Park et al. unpublished (2019)

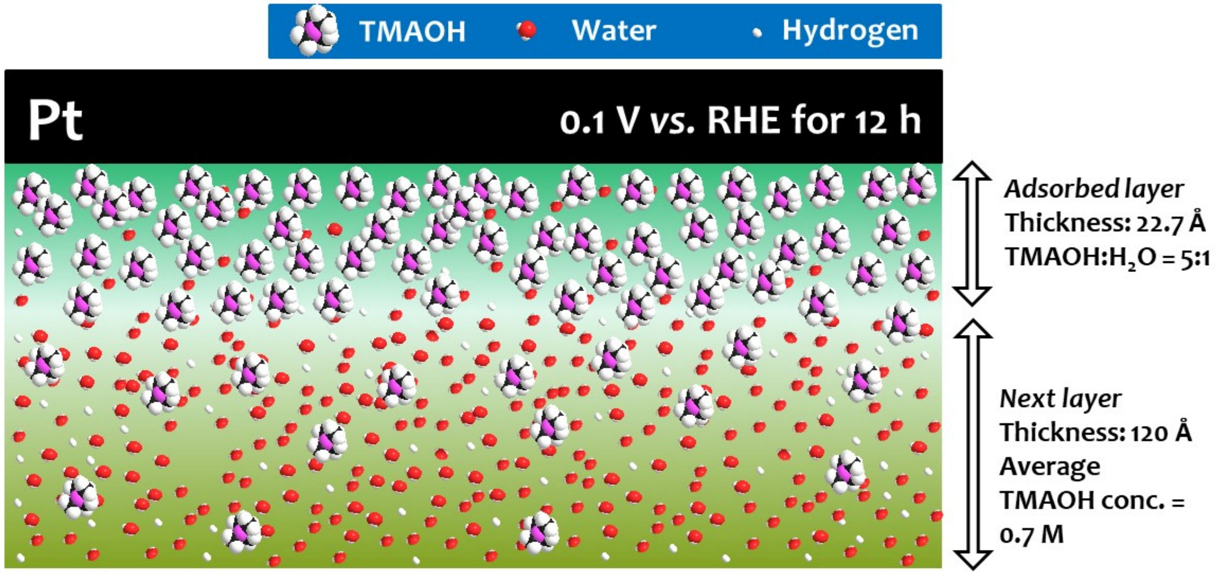
Impact of cation adsorption on HOR catalysts on AMFC Durability

Motivation of cation co-adsorption on AMFC durability

Neutron reflectometry electrochemical cell*



Schematic illustration of co-adsorbed layer structure on Pt after 12 h exposure at 0.1 V vs. RHE

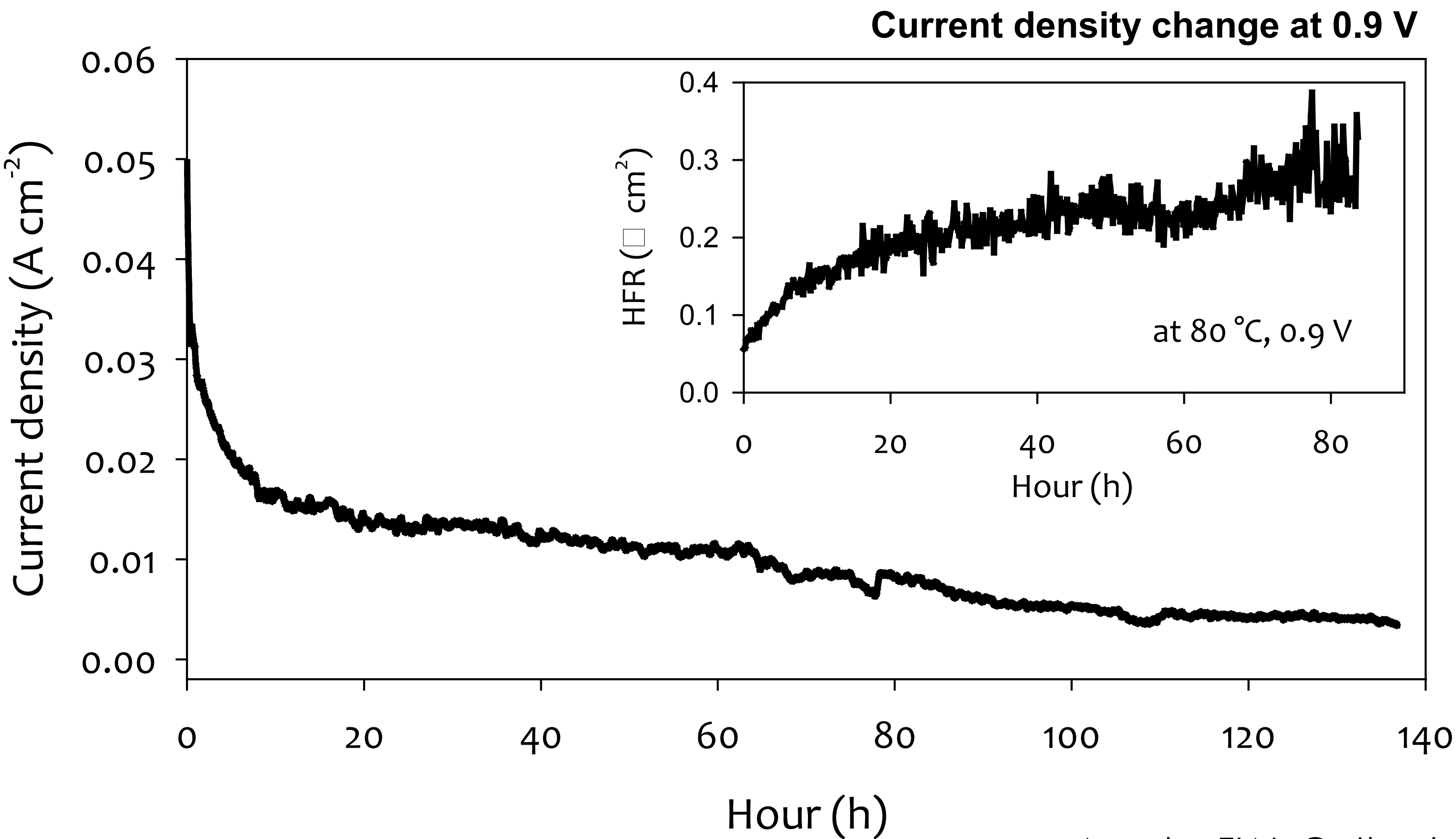


- The concentration of the TMAOH in the co-adsorbed layer calculated from scattering length density is unusually high: the ratio of TMAOH to water = 5:1

(The highest TMAOH to water ratio in the aqueous solution is 1:1)

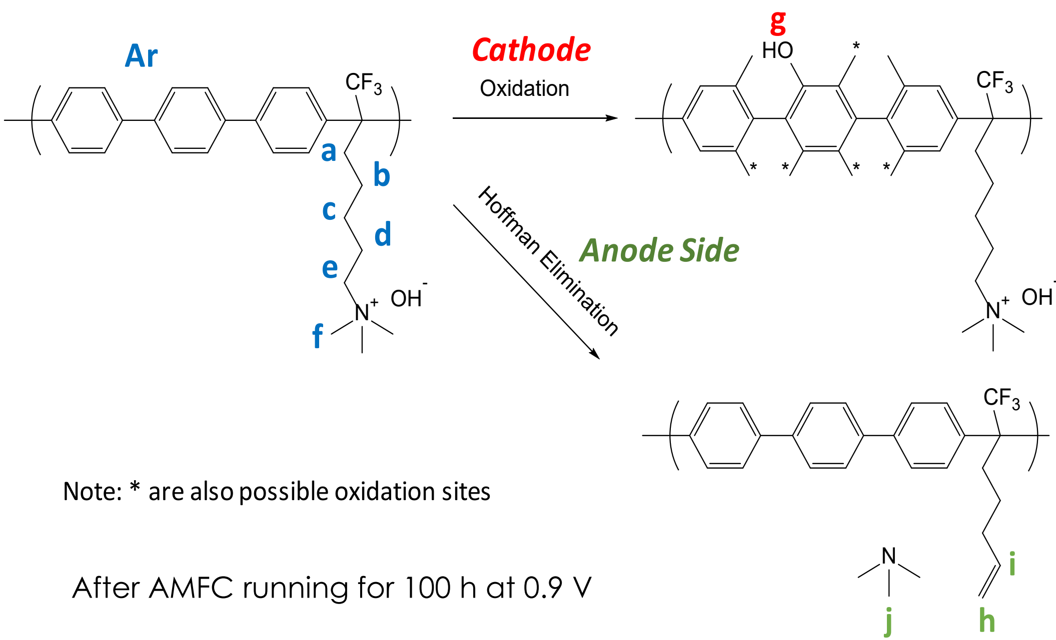
Dumont et al. unpublished data (2019)

Impact of coadsorption on AMFC life



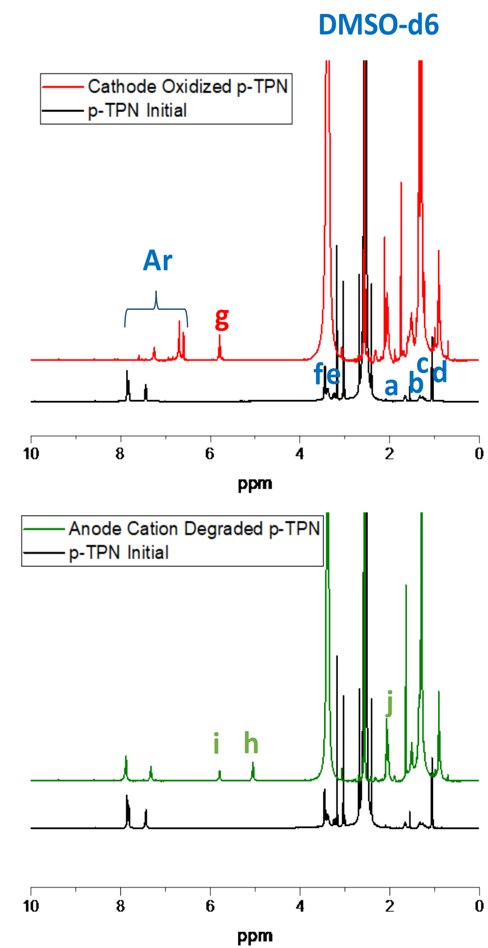
Anode: FLN, Cathode: FLN
both are phenyl non-adsorbing

The ionomer degradation due to the cation co-adsorption



Note: * are also possible oxidation sites

After AMFC running for 100 h at 0.9 V

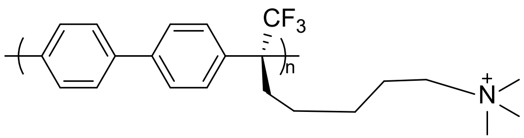


- Cathode ionomer degradation = 30% of the aromatic groups *via* phenyl oxidation.
- Anode ionomer degradation = 27% of the TMA cationic groups *via* Hoffman Elimination.

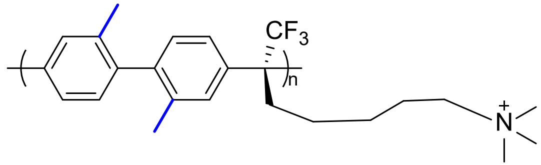
Lee et al. unpublished data (2019)

Water management issue driven by the co-adsorption

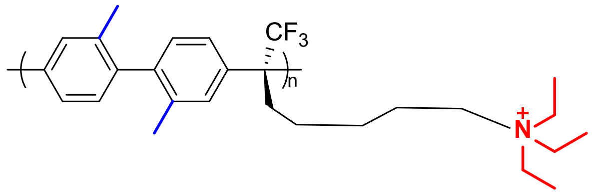
(a) BPN



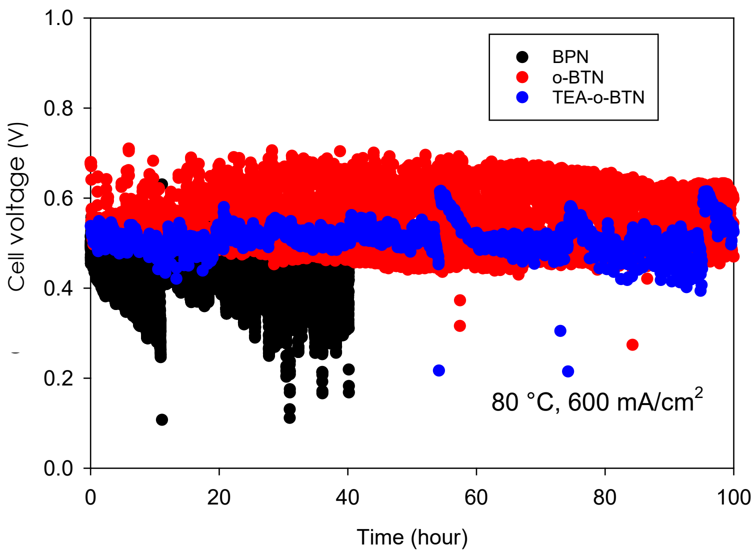
(b) *o*-BTN



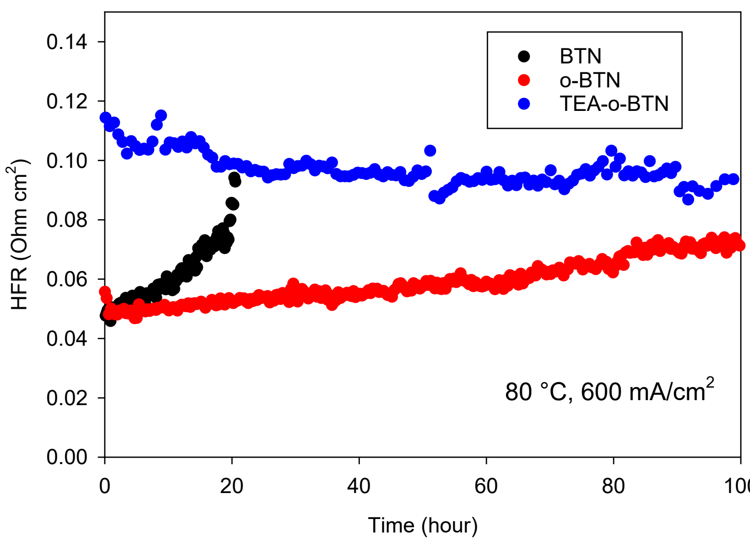
(c) TEA-*o*-BTN



Cell voltage change at 0.6 A/cm²

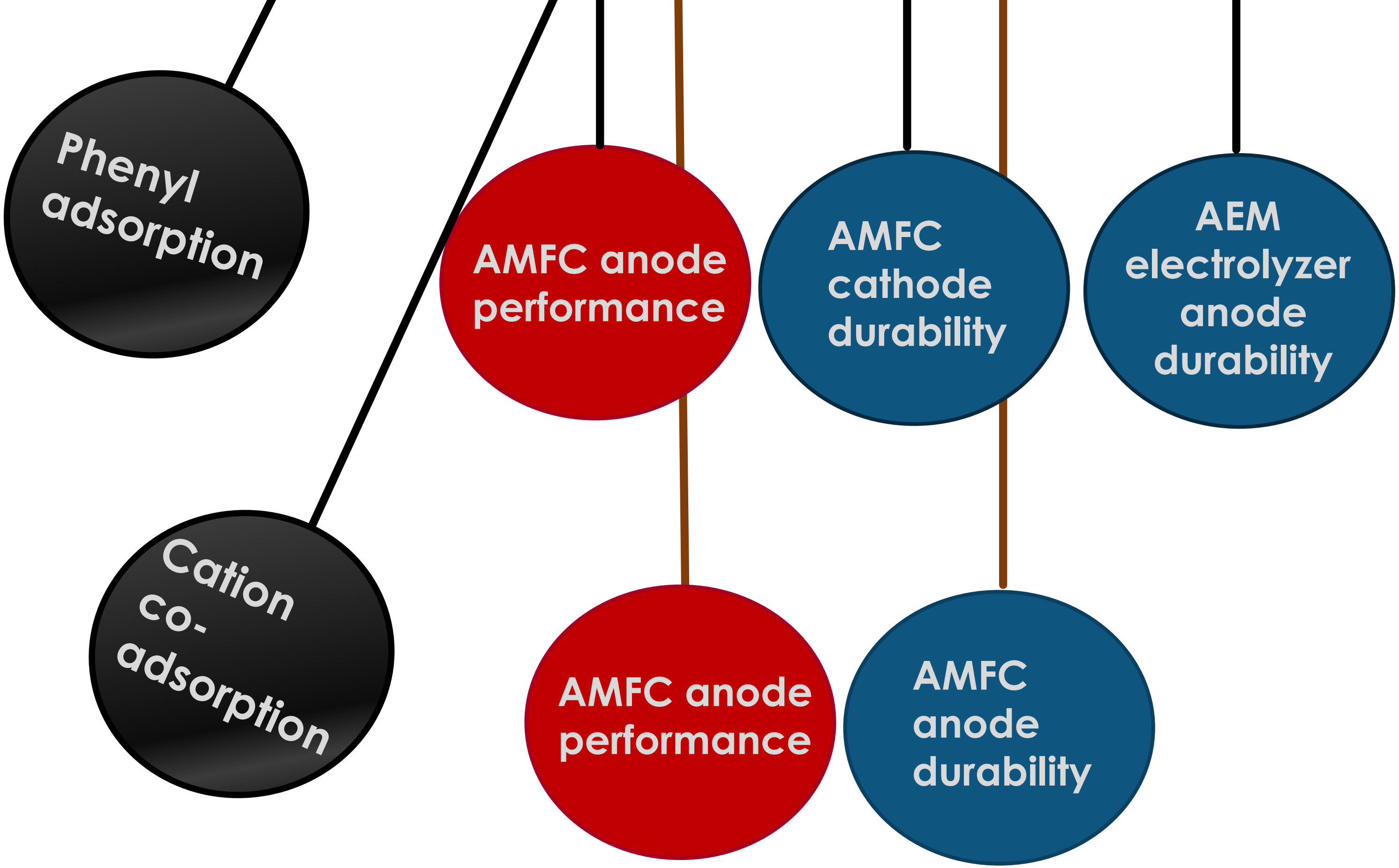


HFR change at 0.6 A/cm²



Maurya et al. unpublished data (2019)

Summary


Phenyl adsorption
Cation co-adsorption
AMFC anode performance
AMFC anode performance
AMFC cathode durability
AMFC anode durability
AEM electrolyzer anode durability

Electrode performance discussion

- **Subject**
  - Ionomer performance
  - Low PGM performance
  - Non PGM performance
  - Electrode processing
  - Liquid electrolyte

- **Area**
  - Fuel cells (HOR and ORR)
  - Electrolyzers (HER and OER)