Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

From Kinetics to Cathode Layer Design: Establishing Targets for Cathodes in Anion-Exchange Membrane Electrolyzers

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The Pt contents of low-surface-area catalyst (LSAC) and high surface area catalyst (HSAC) were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5800). Brunauer-Emmett-Teller (BET) surface area were measured on Micromeritics Tri-Star II 3020 Surface Area and Porosity Analyzer using N_2 adsorption curve branch. The powder X-ray diffractometer (XRD) was tested on the Bruker D8 advance powder X-ray instrument, using Cu Ka radiation. The scanning range is 10-90 °, and the scanning speed is 5 °/min. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed on rotating disc electrode (RDE, Pine Research Rotator) with an electrochemical workstation (Chenhua, CHI660E) in 1 mol/L KOH. The electrochemical active surface area (ECSA) was calculated from the CV curve.

Table S1. Pt content, BET area, XRD size and ECSA for LSAC and HSAC

Catalyst	Pt content wt.%	BET area $m^2/g_{catalyst}$	XRD size nm	ECSA m^2/g_{Pt}
LSAC	46.7	87.2	2.5	25.1
HSAC	47.0	336.6	2.8	45.0

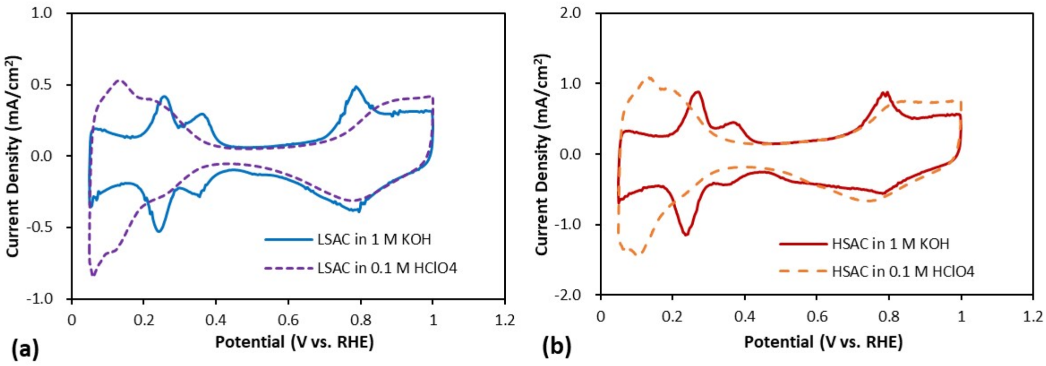

Fig. S1. CV curves for LSAC (a) and HSAC (b) tested in 1 mol/L KOH and 0.1 mol/L $HClO_4$ electrolyte at room temperature with Pt loading of 0.047 mg_{Pt}/cm^2.

The ESCA of LSAC and HSAC was determined to be 42.1 and 78.9 cm^2/g_{Pt}, respectively, from the CV curves in 0.1 mol/L $HClO_4$ (Fig. S1). The differences in ESCA obtained under acidic and alkaline conditions (Table S1) have also been reported in literature.[1] Although the ESCA values are different, The ESCA ratio of HSAC and LSAC is approximately 2 times. Accordingly, all roughness-factor (RF) calculations in the main text uniformly employ ECSA values measured 1 mol/L KOH conditions.

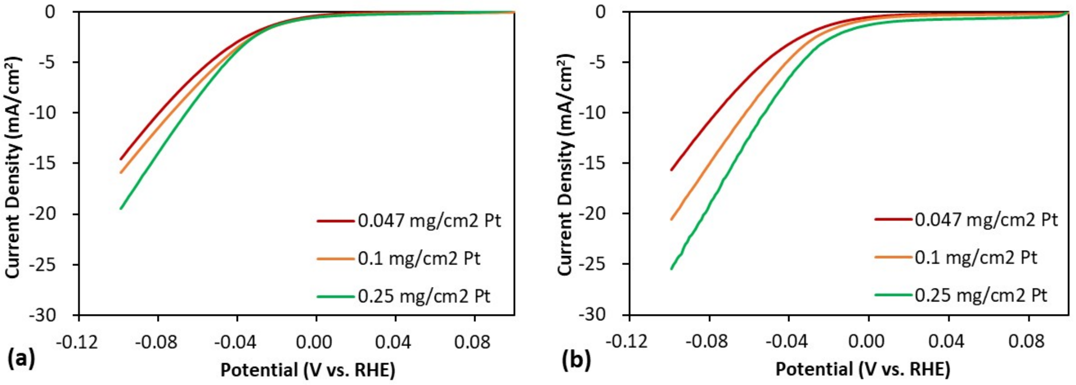

Fig. S2. LSV curves for LSAC (a) and HSAC (b) tested in 1 mol/L KOH with different Pt loading.

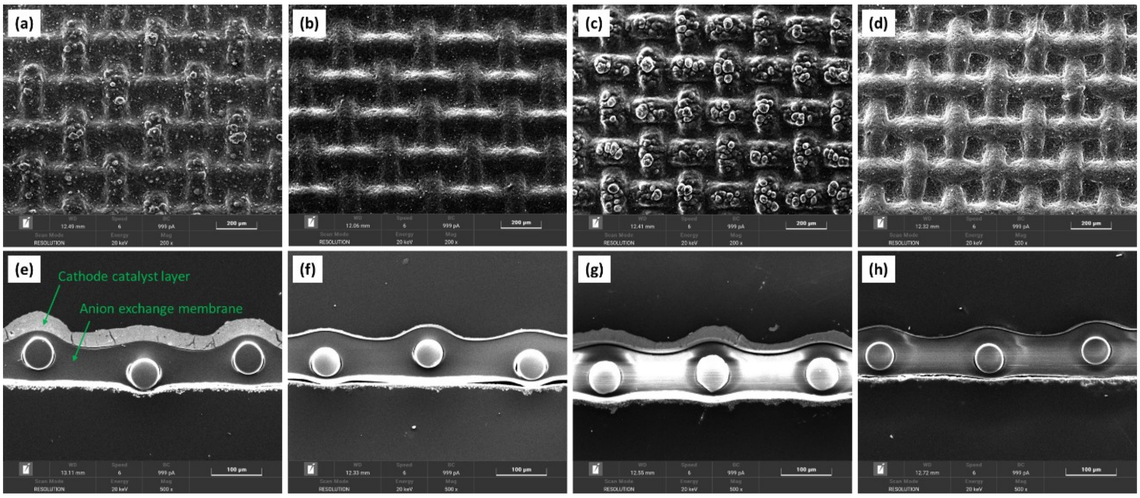

Fig. S3. SEM images for cathode layer with different Pt loading (a) LSAC with 1.1 mg_{Pt}/cm^2, (b) LSAC 0.21 mg_{Pt}/cm^2, (c) HSAC 0.87 mg_{Pt}/cm^2, (d) HSAC 0.19 mg_{Pt}/cm^2. And cross section SEM images for cathode layer with different Pt loading (e) LSAC with 1.1 mg_{Pt}/cm^2, (f) LSAC 0.21 mg_{Pt}/cm^2, (g) HSAC 0.87 mg_{Pt}/cm^2, (h) HSAC 0.19 mg_{Pt}/cm^2.

The SEM cross section images of LSAC and HSAC were obtained (Fig. S3). The LSAC design shows ~5.6x change in thickness (32 vs. 5.7 µm) following an ~5.2x change in loading (1.1 vs. 0.21 mg_{Pt}/cm^2), and the HSAC design shows ~ 5.1x change in thickness (22.6 vs. 4.4 µm) following an ~ 4.6x in loading (0.87 vs. 0.19 mg_{Pt}/cm^2).

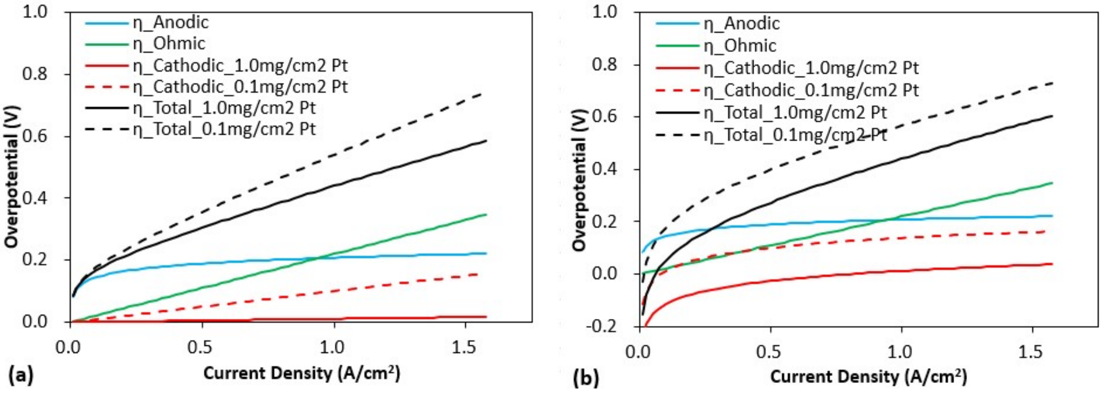

Fig. S4. Voltage loss breakdown plots for the LSAC using the LFA (a) and HFA (b) with high (1.0 mg_{Pt}/cm^2) vs. low (0.1 mg_{Pt}/cm^2) Pt loadings.

Example of how to apply the model to non-PGM catalysts

To briefly demonstrate the applicability of this model to non-PGM catalysts, a new catalyst coated membrane (CCM) was fabricated in this study using Raney Ni as the cathode catalyst with a loading of 1 mg/cm^2. Studies have confirmed that the catalytic activity of this catalyst for the hydrogen evolution reaction (HER) in alkaline media is significantly lower than that of the Pt/C catalyst.[2, 3] To obtain the difference in $i_{o,HER,Apparent}$ for these two catalysts, 3-electrode testing was performed on a 0.1 mg$_{Pt}$/cm^2 (LSAC) and 0.1 mg$_{Raney\ Ni}$/cm^2 sample (Fig. S5 (a)). The cathodic branch of the Butler-Volmer equation was then fit to the HER data of the 0.1 mg$_{Raney\ Ni}$/cm^2 by adjusting only the $i_{o,HER,Apparent}$, and using the values listed in Table S2. Next, while keeping all other parameters constant, the $i_{o,HER,Apparent}$ was adjusted to achieve the best fit to the data obtained for the 0.1 mg$_{Pt}$/cm^2 sample, showing a factor of ~35x difference in activity. From Fig. 8 (c), it is evident that a change in $i_{o,HER,Apparent}$ of 35x requires the HFA to be appropriately modelled at the MEA-level. Thus, starting with the MEA data for the LSAC at 1 mg$_{Pt}$/cm^2 as a baseline, predicted MEA data for the Raney Ni design was obtained using Equation 4 and Equation 6 (as in Section 3.3.2.) by decreasing the $i_{o,HER,Apparent}$ by 35x. As shown in Fig. S5 (b), while the fit is not perfect, the data does indicate that this approach does a reasonable job of predicting how HER catalyst activity differences will be manifested at the MEA-level even for a completely different class of catalyst.

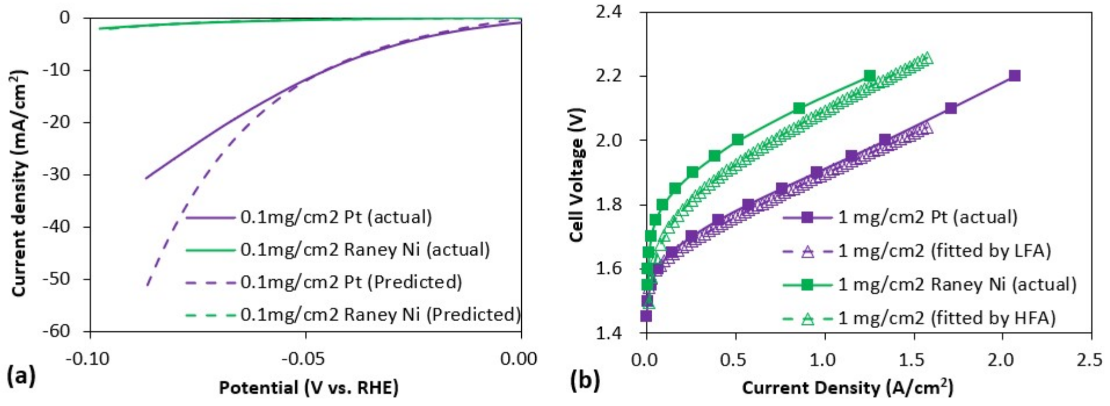

Fig. S5. The Model relationship between Pt-based catalyst of LSAC and non-PGM catalyst of Raney Ni (a) for 3-electrode test and (b) for MEA test.

Relevant Equations

Equation S1 is the standard form of the Butler Volmer (BV) equation, with the only exception being the use of $i_{o,Apparent}$ which is used here since the units of current measured during the polarization curve are A/cm$^2_{\mathrm{MEA}}$, rather than A/cm$^2_{\mathrm{Pt.}}$

$$i = i_{o,Apparent}\left(e^{\frac{\alpha_{anodic}\eta F}{RT}} - e^{-\frac{\alpha_{cathodic}\eta F}{RT}}\right) \tag{S1}$$

Here, α_{anodic} and $\alpha_{\mathrm{cathodic}}$ represent the anodic and cathode transfer coefficients, respectively. This generalized form the of the Bulter Volmer equation is used to express multi-electron transfer reactions, and the 'transfer coefficients' are not to be confused with the 'symmetry factor', often denoted as β, for single electron transfer reactions.[4] As there is no analytical solution to Equation S1, two simplifications are often used based on whether the electrode is experiencing relatively high, or relatively low, polarization. In the case of low polarization, termed LFA here, the BV can be linearized by utilizing the Maclaurin series expansion up to the first order term.

Table S2. Model inputs for the HER for both the LFA and HFA

HER Parameters	LSAC		HSAC		Unit
	LFA	HFA	LFA	HFA	
α_{anodic}	0.5	0.5	0.5	0.5	#
$\alpha_{cathodic}$	0.5	0.5	0.5	0.5	#
$i_{o,\ HER}$	0.00985	0.0032	0.0106	0.0266	A/cm^2
Loading	1	1	0.86	0.86	mg_{Pt}/cm^2
$i_{o,\ Apparent}$	2.46	0.8	4.11	1.03	A/cm^2
ECSA	25	25	45	45	m^2/g_{Pt}

Table S3. Model inputs for the OER for both the LFA and HFA approaches

OER Parameters	Value	Unit
α_{anodic}	1	#
$\alpha_{cathodic}$	1	#
ECSA*	84	m^2/g
Loading	1	$mg_{catalyst}/cm^2$
$i_{o,\ OER}$	0.0002	A/cm^2
$i_{o,OER,\ Apparent}$	0.0005	A/cm^2

* The value of ECSA was approximated from BET specific surface area for the anode catalyst.

References

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