

Supplementary Material for: Biomass potential for producing power via green hydrogen

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S.1 Modelling an Alembic

Table S1 Characteristics of the 304 stainless steel tank alembic

Stage	Parameter	Unit	Value
Pot (Stage 1)	Volume	L	24
	Diameter	m	0.30
	Average duty	kW	1.3
Condenser (Stage 2)	Water cooling flow rate	kg/h	212.4
	Condenser diameter	m ²	0.039
	Water inlet temperature	°C	18
	Condenser pressure	bar	0.76

Table S2. ANOVA of the regression model for the prediction of the final ethanol content

Source	Degree of freedom	Adj SS	Adj MS	F value	P value
Model	9	1522.54	169.17	105.24	0.000
Linear	3	1491.33	497.11	309.24	0.000
A	1	5.28	5.28	3.29	0.130
B	1	1315.85	1315.85	818.57	0.000
C	1	170.20	170.20	105.88	0.000
Square	3	26.94	8.98	5.59	0.047
A ²	1	0.55	0.55	0.34	0.583
B ²	1	16.48	16.48	10.25	0.024
C ²	1	12.47	12.47	7.76	0.039
2-way interaction	3	4.27	1.42	0.89	0.508
A*B	1	2.25	2.25	1.40	0.290
A*C	1	0.06	0.06	0.04	0.851
B*C	1	1.96	1.96	1.22	0.320
Error	5	8.04	1.61		
Lack of fit	3	7.54	2.51	10.05	0.092
Pure error	2	0.50	0.25		
Total	14	1530.58			

A: Power; B: Initial ethanol content (vol.%); C: Volume (L)

$$y = -43.3 + 0.128A + 5.11B + 9.12C - 0.0075AB - 0.0025AC + 0.0875BC - 0.00062A^2 - 0.132B^2 - 0.459C^2 \quad \text{Eq. (S1-1)}$$

S.2 Validation of ESR

Table S3 Kinetic parameters of the ESR over monoliths washcoated with RhPt/CeO₂-SiO₂

Reaction	Energy activation (kJ/mol)	k
Ethanol decomposition	91.0	2.63x10 ⁵
Water gas shift	12.3	2.45x10 ⁷
Methane steam reforming	91.9	3.65x10 ⁷
Methane steam reforming	111.12	9.6x10 ⁷

Table S4 Comparison between experimental and Aspen Plus® data for H₂ and CO yield over a washcoated monolith with RhPt/CeO₂-SiO₂

T (°C)	H ₂ yield		CO yield	
	Experimental	Aspen Plus	Experimental	Aspen Plus
600	2.61	2.76	1.05	1.07
650	3.54	3.43	1.15	1.11
700	3.90	3.98	1.14	1.16

Table S5 Statistical results for the steam reforming process

Statistics parameters	H ₂ yield	CO yield
Pearson correlation coefficient	0.98	0.84
Levene's test for equality of variances	0.082	0.366
Significance	0.788	0.578

S.3 Validation of CO-removal process

Table S6. Kinetic parameters for the removal of CO over washcoated monoliths with Au-Cu/CeO₂

Reaction	Energy activation (kJ/mol)	k (kmol/m ³)
Preferential oxidation of CO	17	1.0x10 ⁴
Water gas shift reaction	60	4.0x10 ⁷
H ₂ oxidation	43	9.9x10 ⁶

Table S7 Comparison between experimental and Aspen Plus® data for H₂ and CO conversion over a washcoated monolith with Au-Cu/CeO₂

T (°C)	H ₂ conversion		CO conversion	
	Experimental	Aspen Plus	Experimental	Aspen Plus
100	0.000	0.014	0.111	0.115
140	-0.001	-0.001	0.250	0.350
180	0.034	-0.022	0.755	0.756
220	0.069	0.038	0.921	0.986
260	0.092	0.134	0.965	1.000
300	0.107	0.196	0.986	1.000

Table S8 Statistics results for CO-removal validation

Statistics parameters	H ₂ conversion	CO conversion
Pearson correlation coefficient	0.857	0.994
Levene's test for equality of variances	3.188	0.012
Significance	0.104	0.915

S.4. Modelling of high temperature proton exchange membrane fuel cell (HT-PEMFC)

Table S9 Materials, transport phenomena, and thermodynamic parameters for a HT-PEMFC

Parameter	Symbol	units	Value
Thickness of the anode and cathode gas diffusion layer	t_{GDL}	m	0.0002
Thickness of the anode and cathode catalyst layer	t_{CL}	m	2.50E-9
Thickness of the membrane	t_m	m	4.00E-5
Membrane	NA	NA	PBI
Binder	NA	NA	PVDF
Thin film electrolyte	NA	NA	H ₃ PO ₄
Weight percentage of phosphoric acid	w^{PA}	wt%	85.0
GDL porosity	ε	Unitless	0.5
Tortuosity	τ	Unitless	1.0
Proton conductivity of electrolyte	σ	S/cm	0.1913
GDL electric conductivity	σ_e	S/cm	6.8750
Anode activation energy	$E_{a,a}$	J/mol.K	16,900
Cathode activation energy	$E_{a,c}$	J/mol.K	72,400
Anode reference temperature	$T_{ref,a}$	°C	160
Cathode reference temperature	$T_{ref,c}$	°C	150
Reference H ₂ concentration on Pt surface in the anode	$C_{Pt,a}$	mol/cm ³	2.11E-7
Reference O ₂ concentration on Pt surface in the cathode	$C_{Pt,c}$	mol/cm ³	1.07E-7
Anode reference exchange current density	$i_{0,A}$	A/cm ²	0.144
Cathode reference exchange current density	$i_{0,C}$	A/cm ²	2.63E-8
Transfer coefficient in the cathode site	α_c	Unitless	0.75
Transfer coefficient in the anode site	α_A	Unitless	0.50
Anode catalyst surface area	$a_{c,a}$	m ² /g	64
Cathode catalyst surface area	$a_{c,c}$	m ² /g	32.25
Anode catalyst loading	$L_{c,a}$	mg/cm ²	0.2
Cathode catalyst loading	$L_{c,c}$	mg/cm ²	0.4
Anode Pressure	P_A	Atm	1
Cathode Pressure	P_C	Atm	1

Diffusion Transport in Porous media

Table S10 Gas properties

Gas	MW	Tc (K)	Pc (atm)	a	b
H ₂	2	33.191	12.9835	0.0002745	1.832
CO	28	132.951	34.5375	0.0002745	1.832
CO ₂	44	304.201	72.8582	0.0002745	1.832
CH ₄	16	191.061	45.8115	0.0002745	1.832
O ₂	32	154.781	50.1525	0.0002745	1.832
N ₂	28	126.271	33.5484	0.0002745	1.832
H ₂ O	18	647.301	218.2564	0.0003640	2.334

$$D_{i,j}^{EFF} = \frac{a}{P} \left(\frac{T}{\sqrt{T_{c,i}T_{c,j}}} \right)^b (P_{c,i}P_{c,j})^{1/3} (T_{c,i}T_{c,j})^{5/12} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2} \varepsilon^\tau \quad \text{Eq. (S4-1)}$$

Flux of all the species in the anode side is 0, except for H₂, whose molar flux could be calculated according to Eq. (S4-2):

$$N_{H_2} = \frac{j}{2F} \quad \text{Eq. (S4-2)}$$

Flux of the species in the cathode side are given by the following equations, where j is the current density and F is the Faraday constant:

$$N_{N_{2,g}} = 0 \quad \text{Eq. (S4-3)}$$

$$N_{O_{2,g}} = \frac{j}{4F} \quad \text{Eq. (S4-4)}$$

$$N_{H_2O,g} = \frac{-j}{2F} \quad \text{Eq. (S4-5)}$$

The diffusion of the species in the anode side and cathode side is described by Eq. (S4-6)

$$\frac{\delta x_i}{\delta z} = \frac{RT}{P} \sum_j \frac{x_i N_j - x_j N_i}{D_{i,j}^{EFF}} \quad \text{Eq. (S4-6)}$$

When $z = 0$, the initial composition ($x_{i,0}$) will be the content of the dry syngas and air for the anode and cathode, respectively. These compositions are retrieved from Aspen Plus.

Thin electrolyte film model

The oxygen and hydrogen diffusivity in the catalyst layer (cm²/s) is calculated according to Eq. (S4-7) and Eq. (S4-8), respectively. While the Henry constant (mol.m³/atm) for both oxygen and hydrogen is calculated according to Eq (S4-9) and Eq. (S4-10), respectively.

Table S10 shows the parameters for diffusivity and Henry constant of oxygen.

$$D_{O_2}^{PA} = 0.0001 \text{Exp} \left(A(w^{PA})^2 + B(w^{PA}) + C + \frac{D(w^{PA})^2 + E(w^{PA}) + F}{T_{\text{Cell}}} \right) \quad \text{Eq. (S4-7)}$$

$$D_{H_2}^{PA} = 2D_{O_2}^{PA} \quad \text{Eq. (S4-8)}$$

$$H_{O_2}^{PA} = 0.1 \text{Exp} \left(A(w^{PA})^2 + B(w^{PA}) + C + \frac{D(w^{PA})^2 + E(w^{PA}) + F}{T_{\text{Cell}}} \right) \quad \text{Eq. (S4-9)}$$

$$H_{H_2}^{PA} = 4D_{H_2}^{PA} \quad \text{Eq. (S4-10)}$$

To obtain the concentration of oxygen and hydrogen in the electrolyte films, Fick's law is employed as shown in Eq. (S4-11) to (S4-14).

$$C_{H_2, \text{dissolved}} = \frac{x_{H_2} P_{\text{anode}}}{H_{H_2}^{PA}} \quad \text{Eq. (S4-11)}$$

$$C_{O_2, \text{dissolved}} = \frac{x_{O_2} P_{\text{cathode}}}{H_{O_2}^{PA}} \quad \text{Eq. (S4-12)}$$

$$C_{H_2, \text{Pt}} = C_{H_2, \text{dissolved}} - \frac{J_{H_2} \delta_{\text{anode}}}{D_{H_2}^{PA} S_{\text{Pt, anode}}} \quad \text{Eq. (S4-13)}$$

$$C_{O_2, \text{Pt}} = C_{O_2, \text{dissolved}} - \frac{J_{O_2} \delta_{\text{cathode}}}{D_{O_2}^{PA} S_{\text{Pt, cathode}}} \quad \text{Eq. (S4-14)}$$

Electrochemical Modelling

The overall voltage (E) of the fuel cell could be calculated according to Eq. (S4-15), where E_{rev} (Eq S4-16) is the reversible cell voltage, $\eta_{\text{act, a}}$ (Eq. S4-17) and $\eta_{\text{act, c}}$ (Eq. S4-18) are the activation losses in the anode and cathode, respectively. η_{ohm} is the ohmic losses.

a actividad

$$V = E_{\text{rev}} - \eta_{\text{act, a}} - \eta_{\text{act, c}} - \eta_{\text{ohm}} \quad \text{Eq. (S4-15)}$$

$$E_{\text{rev}} = E^\circ + \frac{RT_{\text{Cell}}}{n_{H_2} F} \text{Ln} \left(\frac{(RT_{\text{Cell}})^{1.5} C_{H_2, \text{Pt}} C_{O_2, \text{Pt}}^{0.5}}{a_{H_2O}} \right) \quad \text{Eq. (S4-16)}$$

$$\eta_{\text{act, a}} = \frac{RT_{\text{Cell}}}{\alpha_a F} \text{Sinh}^{-1} \left(\frac{i}{2i_0^A (1 - \theta_{CO})^2} \right) \quad \text{Eq. (S4-17)}$$

$$\eta_{\text{act, c}} = \frac{RT_{\text{Cell}}}{\alpha_c F} \text{Sinh}^{-1} \left(\frac{i}{2i_0^C} \right) \quad \text{Eq. (S4-18)}$$

$$i_0^A = i_{0,ref}^A S_{Pt,anode} \left(\frac{C_{H_2,Pt}}{C_{Pt,A}^{Ref}} \right)^{\gamma_a} \cdot \exp \left(\left(-\frac{E_{c,a}}{RT_{Cell}} \right) \left(1 - \frac{T_{Cell}}{T_{ref,a}} \right) \right) \quad \text{Eq. (S4-19)}$$

$$i_0^C = i_{0,ref}^C S_{Pt,anode} \left(\frac{C_{O_2,Pt}}{C_{Pt,C}^{Ref}} \right)^{\gamma_c} \cdot \exp \left(\left(-\frac{E_{c,c}}{RT_{Cell}} \right) \left(1 - \frac{T_{Cell}}{T_{ref,c}} \right) \right) \quad \text{Eq. (S4-20)}$$

CO poisoning

The effect of CO on the anode side of the fuel cell could be calculated according to Authayanun et al. (Authayanun and Hacker, 2018)

$$\theta_{CO} = a \ln \left(\frac{[CO]}{[H_2]} \right) + b \ln(i) \ln \left(\frac{[CO]}{[H_2]} \right) + c \quad \text{Eq. (S4-22)}$$

$$a = -0.00012784T^2 + 0.11717499T - 26.62908873 \quad \text{Eq. (S4-23)}$$

$$b = 0.0001416T^2 - 0.12813608T - 28.852463626 \quad \text{Eq. (S4-24)}$$

$$c = -0.00034886T^2 + 0.31596903T - 70.11693333 \quad \text{Eq. (S4-25)}$$

Ohmic losses

The ohmic losses could be calculated according to the following equations

$$A = \exp(0.0002T^3 - 0.0132T^2 + 0.2257T + 9.6082) \quad \text{Eq. (S4-26)}$$

$$B = \exp(0.62T^3 - 39.7T^2 + 527T + 26300) \quad \text{Eq. (S4-27)}$$

$$\sigma_m = \frac{A}{T} \exp \left(\frac{-B}{RT} \right) \quad \text{Eq. (S4-28)}$$

$$\eta_{ohm} = \frac{t_m}{\sigma_m} i \quad \text{Eq. (S4-29)}$$

S.5 ANOVA results

Table S11. ANOVA table for all the response variables

Parameter	Power fuel cell (kWh/kg)	Efficiency	Energy consumption (kW/kg)
Model	<0.0001	<0.0001	<0.0001
A	<0.0001	<0.0001	<0.0001
B	0.0017	-	0.0029
C	<0.0001	<0.0001	<0.0001
D	<0.0001	<0.0001	<0.0001
E	0.0021	0.0151	-
A ²	0.0638	0.0022	-
B ²	-	-	-
C ²	<0.0001	<0.0001	<0.0001
D ²	<0.0001	0.0002	-
E ²	0.0139	0.0992	-
AB	-	-	-
AC	0.0022	<0.0001	0.0002
AD	0.0009	-	0.0384
AE	0.0046	0.0562	-
BC	-	-	-
BD	-	-	-
CD	0.0288	0.1191	0.0161
R ²	0.9979	0.9715	0.9988
R ² adjusted	0.9970	0.9622	0.9986
R ² predicted	0.9940	0.9058	0.9970

(-): The variable was excluded by the stepwise method

Table S12. ANOVA table for power production

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0313	13	0.0024	1151.82	< 0.0001	significant
A-EtOH	0.0082	1	0.0082	3936.66	< 0.0001	
B-Load	0	1	0	11.78	0.0017	
C-S/E	0.0218	1	0.0218	10453.17	< 0.0001	
D-ESR	0.0008	1	0.0008	383.76	< 0.0001	
E-CO	0	1	0	11.21	0.0021	
AC	0	1	0	11.09	0.0022	
AD	0	1	0	13.29	0.0009	
AE	0	1	0	9.28	0.0046	
CD	0	1	0	5.24	0.0288	
A ²	7.70E-06	1	7.70E-06	3.69	0.0638	
C ²	0.0003	1	0.0003	128.56	< 0.0001	
D ²	0.0001	1	0.0001	27.84	< 0.0001	
E ²	0	1	0	6.77	0.0139	
Residual	0.0001	32	2.09E-06			
Lack of Fit	0.0001	27	2.48E-06	14028.14	< 0.0001	significant
Pure Error	8.83E-10	5	1.77E-10			
Cor Total	0.0314	45				

Table S13. ANOVA table for the efficiency

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	186.07	11	16.92	105.18	< 0.0001	significant
A-EtOH	15.38	1	15.38	95.62	< 0.0001	
C-S/E	102.29	1	102.29	636.06	< 0.0001	
D-ESR	43.56	1	43.56	270.83	< 0.0001	
E-CO	1.05	1	1.05	6.56	0.0151	
AC	5.26	1	5.26	32.69	< 0.0001	
AE	0.6286	1	0.6286	3.91	0.0562	
CD	0.411	1	0.411	2.56	0.1191	
A ²	1.76	1	1.76	10.93	0.0022	
C ²	16.57	1	16.57	103.06	< 0.0001	
D ²	2.76	1	2.76	17.19	0.0002	
E ²	0.462	1	0.462	2.87	0.0992	
Residual	5.47	34	0.1608			
Lack of Fit	5.47	29	0.1886	18459.96	< 0.0001	significant
Pure Error	0.0001	5	0			
Cor Total	191.54	45				

Table S14. ANOVA table for thermal energy consumption

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.6602	8	0.0825	3963.1	< 0.0001	significant
A-EtOH	0.1797	1	0.1797	8628.94	< 0.0001	
B-Load	0.0002	1	0.0002	10.2	0.0029	
C-S/E	0.4731	1	0.4731	22720.08	< 0.0001	
D-ESR	0.0031	1	0.0031	149.77	< 0.0001	
AC	0.0004	1	0.0004	17.79	0.0002	
AD	0.0001	1	0.0001	4.61	0.0384	
CD	0.0001	1	0.0001	6.37	0.0161	
C ²	0.0035	1	0.0035	167.07	< 0.0001	
Residual	0.0008	37	0			
Lack of Fit	0.0008	32	0			
Pure Error	0	5	0			
Cor Total	0.6609	45				