Supporting Information

High performance lignin flow fuel cell based on self-generating electricity of lignin at low temperature via privileged structure and redox chemistry

Zixin Xie,[a] Xihong Zu,*[a,b] Jinxin Lin,[a] Xueqing Qiu,*[a,b] Tengda Liang [a] and Liheng Chen [a,b]

[a] *Guangdong Provincial Key Laboratory of Plant Resources Biorefinery, School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, 510006, China*

[b] *Jieyang Branch of Chemistry and Chemical Engineering Guangdong Laboratory, Jieyang 515200, China.*

***Corresponding Authors:** Prof. Xihong Zu, Prof. Xueqing Qiu

E-mail address: xhzu@gdut.edu.cn (X. Zu), cexqqiu@scut.edu.cn (X. Qiu).

Supplementary Figures

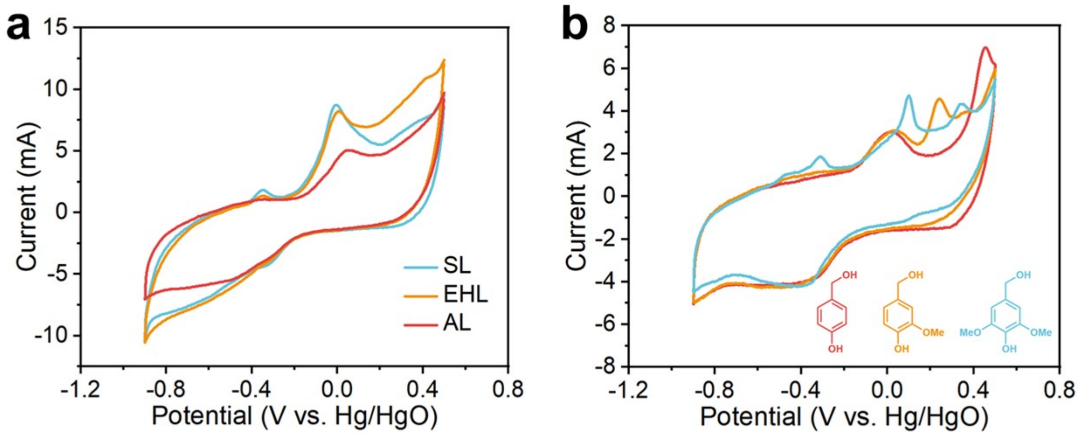

Fig. S1. (a) CV curves of sodium lignosulfonate (SL), enzymatic hydrolysis lignin (EHL) and alkali lignin (AL) in 1 M NaOH solution with 5 g L^{-1} lignin. (b) CV curves of 4-hydroxybenzyl alcohol, 4-hydroxy-3-methoxybenzyl alcohol and 4-hydroxy-3,5-dimethoxybenzyl alcohol in 1 M NaOH solution with 10 mM lignin model compounds.

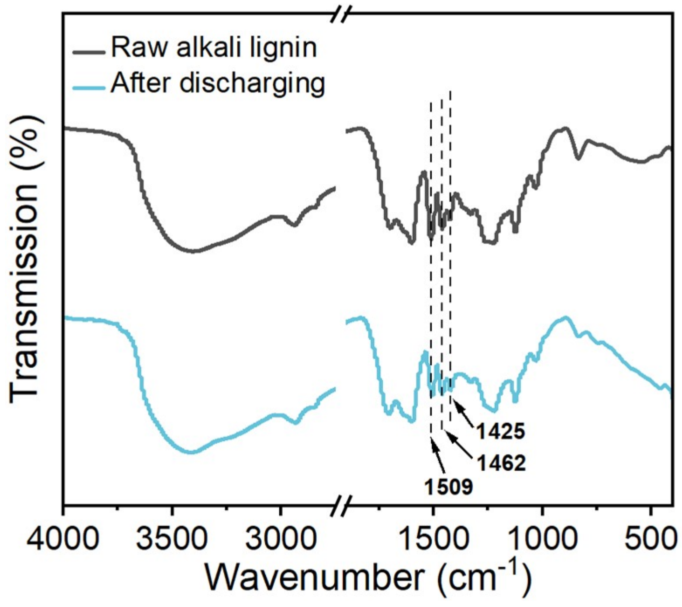

Fig. S2. FTIR spectra of alkali lignin before and after discharging for 4h.

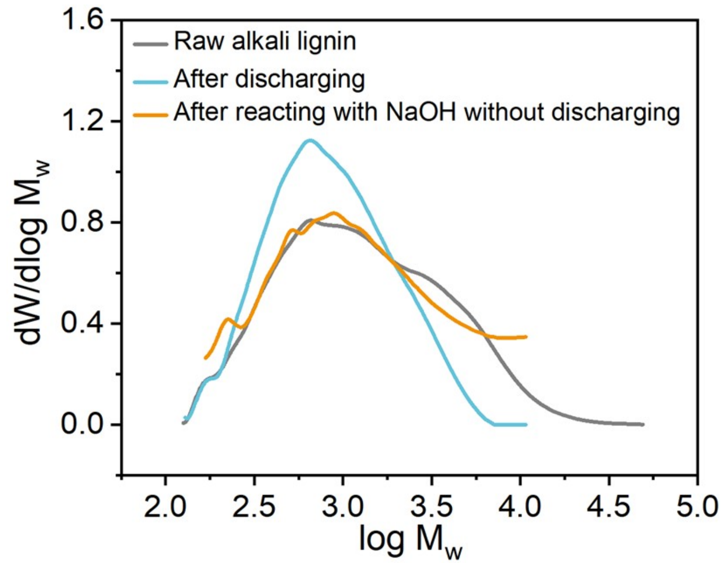

Fig. S3. Molecular weight distribution curves of raw alkali lignin, alkali lignin after discharging for 4h, and alkali lignin after reacting with NaOH solution before discharging.

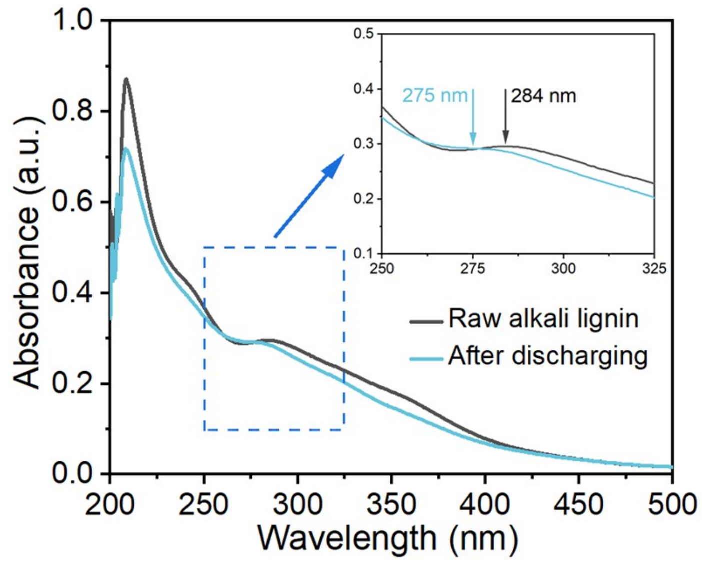

Fig. S4. UV-vis absorbance spectra of alkali lignin before and after discharging for 4h.

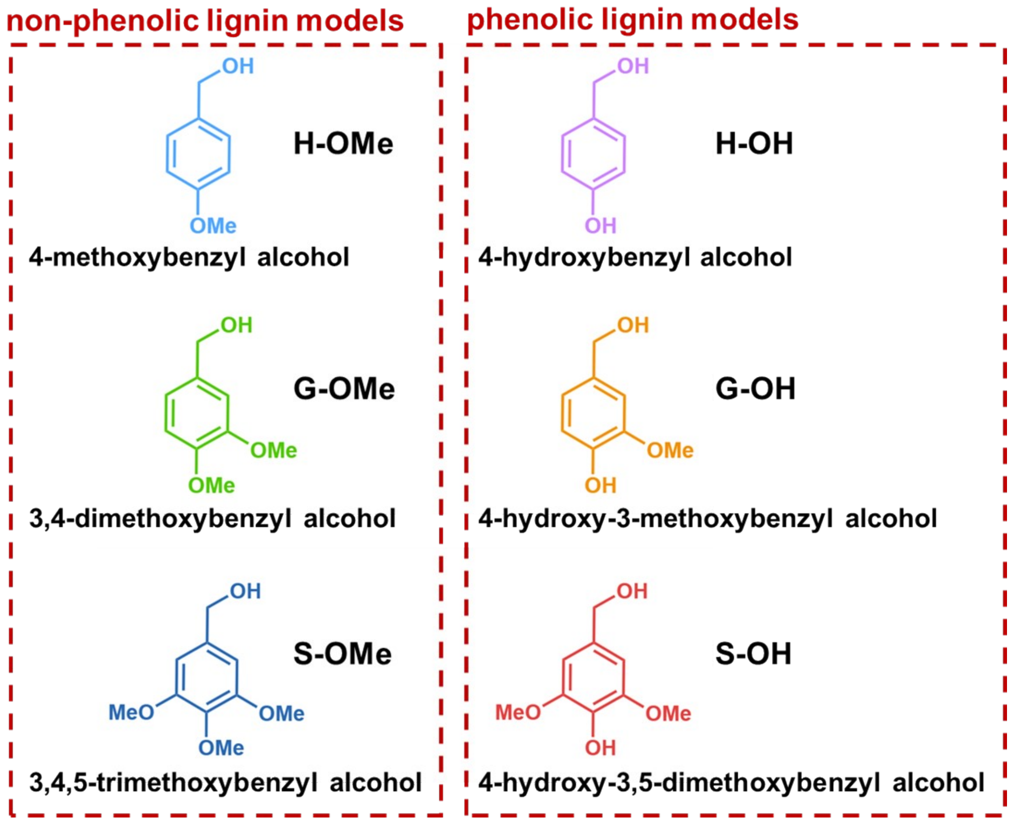

Fig. S5. Selected non-phenolic and phenolic lignin model compounds.

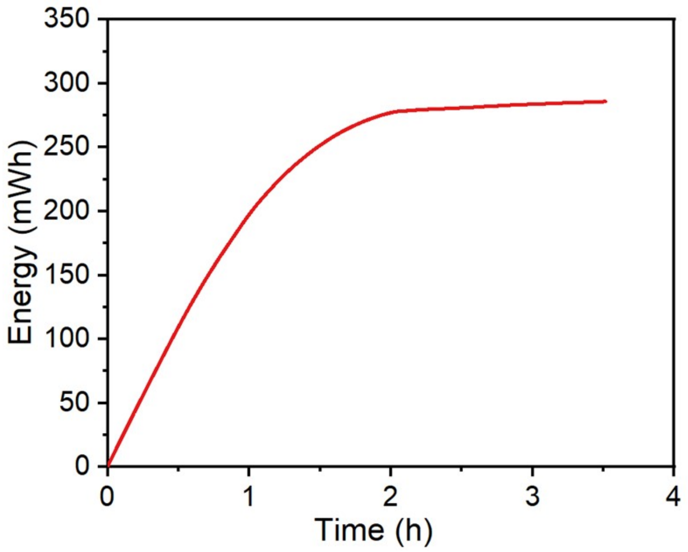

Fig. S6. Quantitative analysis of electricity generation from 4-hydroxy-3,5-dimethoxybenzyl alcohol (S-OH). Output energy of the LFFC tested by the constant-voltage (0.3V) discharging method (50 mL solution containing 0.5 g S-OH and 2 mol L^{-1} NaOH).

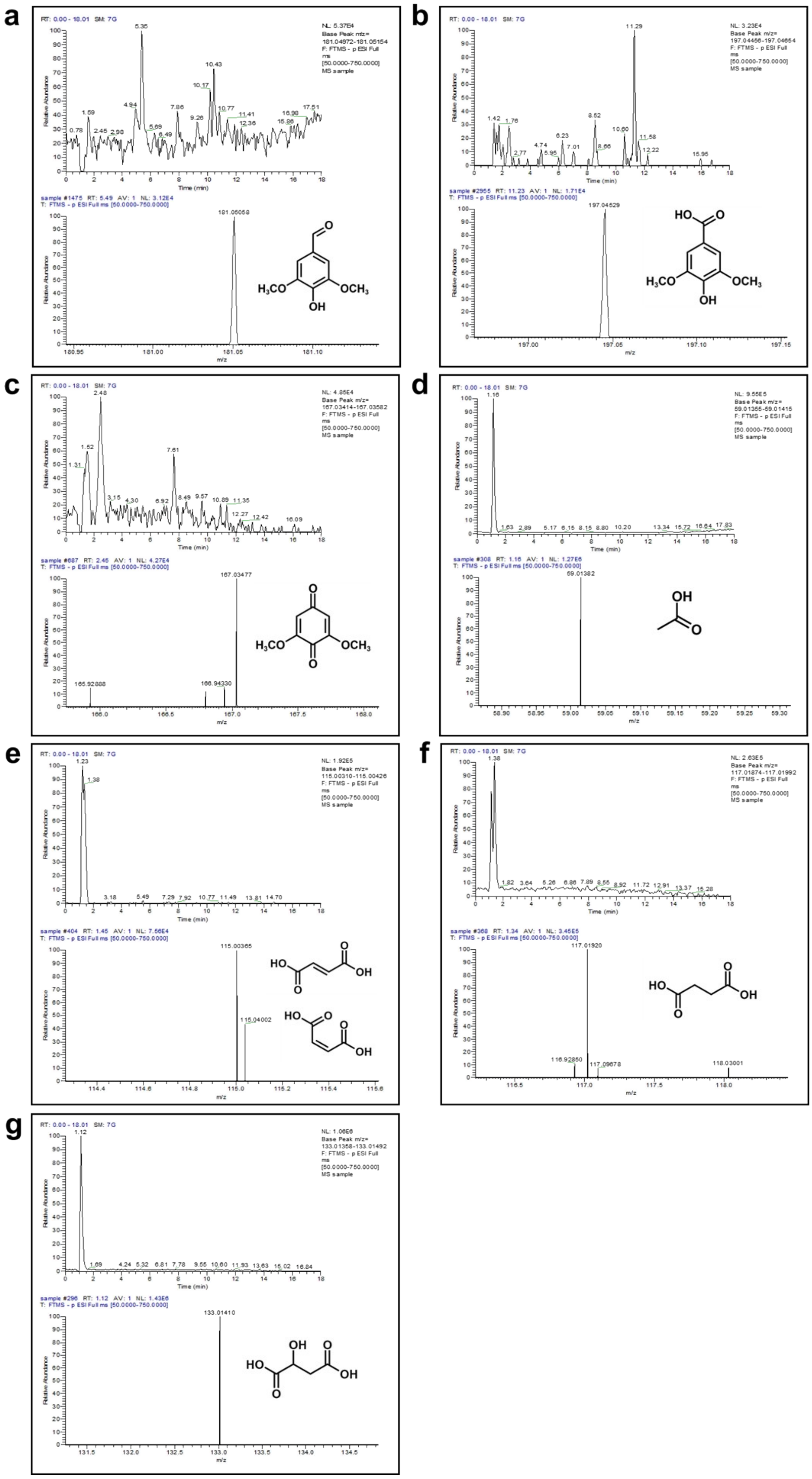

Fig. S7. HPLC-MS analysis of the liquid products when S-OH was discharged for 3.5 h at 90°C (50 mL solution containing 0.5 g S-OH and 2 mol L^{-1} NaOH).

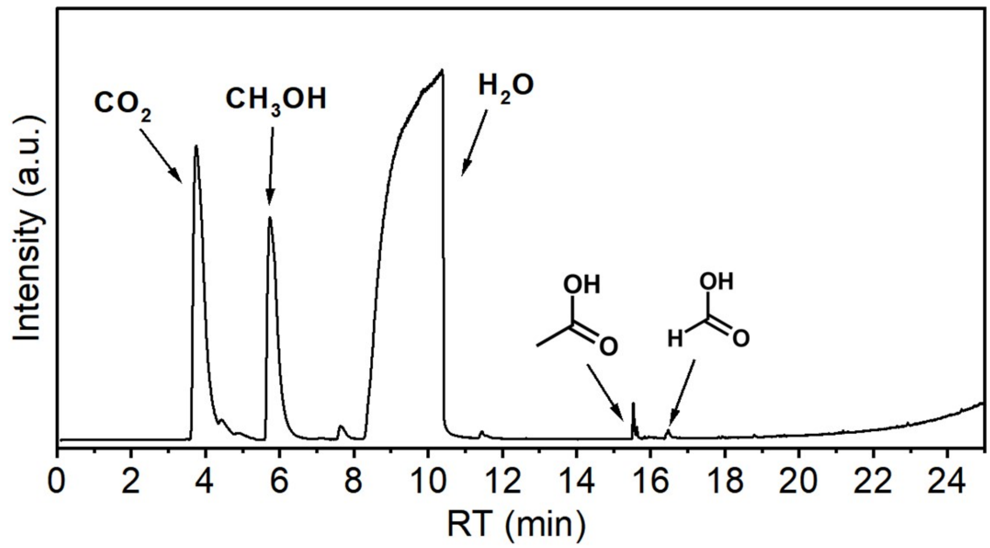

Fig. S8. HS-GC-MS analysis of the liquid products when S-OH was discharged for 3.5 h at 90℃ (50 mL solution containing 0.5 g S-OH and 2 mol L^{-1} NaOH).

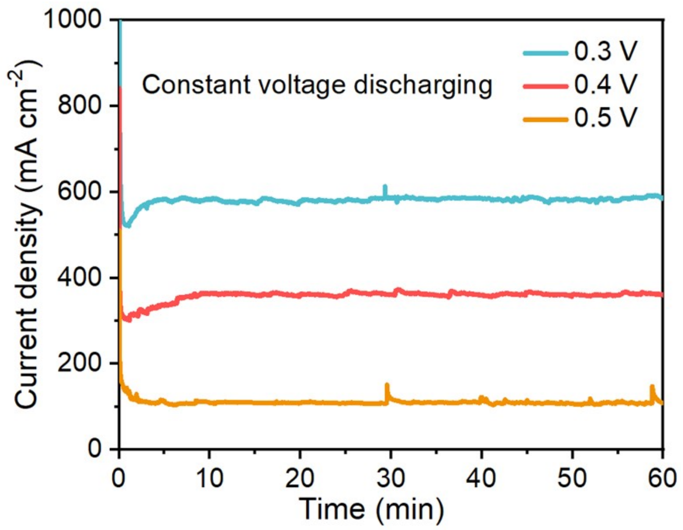

Fig. S9. Continuous discharge performance of the LFFC fueled by alkali lignin at different constant voltages.

Supplementary Tables

Table S1. The NMR assignments of major signals in 2D-HSQC NMR spectra of alkali lignin samples.

Label	δ_C/δ_H (ppm)	Assignments
$-OCH_3$	56.4/3.70	C-H in methoxyls
A_α	71.6/4.86	C_α-H_α in β-O-4 substructures (A)
A_β	86.9/4.11	C_β-H_β in β-O-4 substructures (A)
A_γ	59.9/3.60	C_γ-H_γ in β-O-4 substructures (A)
B_α	87.5/5.56	C_α-H_α in phenylcoumaran substructures (B)
B_γ	62.3/3.76	C_γ-H_γ in phenylcoumaran substructures (B)
C_α	85.1/4.45	C_α-H_α in β-β resinol substructures (C)
C_γ	70.7/3.45	C_γ-H_γ in β-β resinol substructures (C)
SD	82.1/4.92	C-H in β-1 spirodienone substructures (SD)
Gly_β	75.5/3.48	C_β-H_β in arylglycerol substructures (Gly)
Gly_γ	62.7/3.16-3.46	C_γ-H_γ in arylglycerol substructures (Gly)
$S_{2,6}$	104.5/6.72	$C_{2,6}$-$H_{2,6}$ in syringyl units (S)
$S'_{2,6}$	106.3/7.28	$C_{2,6}$-$H_{2,6}$ in oxidized syringyl units (S’)
G_2	111.0/6.99	C_2-H_2 in guaiacyl units (G)
G'_2	112.1/7.38	C_2-H_2 in guaiacyl units (G’)
G_5	115.3/6.68	C_5-H_5 in guaiacyl units (G)
G_6	119.1/6.75	C_6-H_6 in guaiacyl units (G)
$H_{2,6}$	128.7/7.23	$C_{2,6}$-$H_{2,6}$ in *p*-hydroxyphenyl units (H)
FA_2	111.3/7.25	C_2–H_2 in ferulate (FA)
FA_6	122.3/7.12	C_6–H_6 in ferulate (FA)
FA_α	144.6/7.45	C_α-H_α in ferulate (FA)
FA_β	116.9/6.39	C_β-H_β in ferulate (FA)
$pCA_{2,6}$	130.3/7.49	$C_{2,6}$-$H_{2,6}$ in p-coumaroylated substructures (*p*CA)
pCA_α	144.6/7.45	C_α-H_α in p-coumaroylated substructures (*p*CA)
$pCA_{3,5}$	116.9/6.39	$C_{3,5}$-$H_{3,5}$ in p-coumaroylated substructures (*p*CA)
pCA_β	116.9/6.39	C_β-H_β in p-coumaroylated substructures (*p*CA)

Table S2. Molecular weight of lignin.

Samples	Mw (g/mol)	Mn (g/mol)	PDI
Raw alkali lignin	2257	777	2.9048
After reacting with NaOH solution before discharging	2018	733	2.7531
After discharging	1143	632	1.8085

Table S3. Hydroxyl group content of alkali lignin before and after discharging.

Samples	Aliphatic OH	C_5-substituted OH		Guaiacyl OH	p-Hydroxyphenyl OH	Total phenolic OH	Carboxylic acid OH
		Condensed OH	Syringyl OH				
Raw alkali lignin	1.33	0.14	0.21	0.44	0.34	1.13	0.08
After discharging (4h)	0.53	0.18	0.12	0.33	0.16	0.79	0.54

Note: The hydroxyl group content was determined by ^{31}P NMR.

Table 4. Hydroxyl group content of different types of lignin.

Samples	Aliphatic OH	C_5-substituted OH		Guaiacyl OH	p-Hydroxyphenyl OH	Total phenolic OH	Carboxylic acid OH
		Condensed OH	Syringyl OH				
AL	1.33	0.14	0.21	0.44	0.34	1.13	0.08
EHL	1.52	0.48	0.35	0.39	0.43	1.65	0.37
SL	1.45	0.32	0.01	0.44	0.15	0.92	3.26

Note: The hydroxyl group content was determined by ^{31}P NMR.

Table S5. Comparison of the generated electric energy (based on 1.0g biomass) of different biomass flow fuel cells.

Fuel cell types	Fuels in anode half-cell	Electron mediators in anolyte	Electron mediators in catholyte	External processing or pretreatment	Electric energy (mWh)	Ref.
BFFC	Wheat straw	PMo_9V_3	$FeCl_3$	The suspension was heated in an autoclave at 120 °C for 1 h.	24.6	1
BFFC	Sugarcane bagasse	$FeCl_3$	$FeCl_3$	The suspension was heated in an autoclave at 120 °C for 30 min.	101.4	2
BFFC	Sugarcane bagasse	$K_3[Fe(CN)_6]$	$FeCl_3$	The suspension was heated in an autoclave at 120 °C for 30 min.	28.9	2
BFFC	Sodium lignosulfonate	$CuCl_2/TiOSO_4$	$(VO_2)_2SO_4$	The solution was heated to 90°C under stirring to react 1 h.	116.24	3
LFFC	**Alkali lignin**	**None**	**$(VO_2)_2SO_4$**	**None**	**219.9**	**This work**

Table S6. Comparison of the discharge performance of different biomass flow fuel cells.

Fuel cell types	**Fuels in anode half-cell**	**Electron mediators in anolyte**	**Electron mediators in catholyte**	**External processing or pretreatment**	**Open-circuit voltage (V)**	**Peak power Density (P_{max}, mW/cm^2)**	**Ref.**
BFFC	Wheat straw	PMo_9V_3	$FeCl_3$	The suspension was heated in an autoclave at 120 °C for 1 h.	0.44	44.7	1
BFFC	Sugarcane bagasse	$K_3[Fe(CN)_6]$	$FeCl_3$	The suspension was heated in an autoclave at 120 °C for 30 min.	0.78	75.4	2
BFFC	Sodium lignosulfonate	$CuCl_2/TiOSO_4$	$(VO_2)_2SO_4$	The solution was heated to 90°C under stirring to react 1 h.	0.58	55.1	3
BFFC	Cellulose	$H_3PMo_{12}O_{40}$ (PMo_{12})	Pt (60%)/C catalyst	The solution was irradiated by simulated sunlight and heated on a hotplate up to 95 °C and kept for 6 h.	0.38	0.72	4
BFFC	Raffinose	$H_3PMo_{12}O_{40}$ (POM-I)	$H_{12}P_3Mo_{18}V_7O_{85}$ (POM-II)	The solution was irradiated with simulated sunlight for 8 h.	0.51	45	5
BFFC	Wheat straw	$FeCl_3$	$(VO_2)_2SO_4$	The suspension was heated to reflux at 100 °C under stirring for 20 h.	0.61	100	6
BFFC	Wheat straw	Methylene blue (MB)	$FeCl_3$	The suspension was heated in an oil bath at 90-105 °C.	1.56	41.8	7
BFFC	Sodium lignosulfonate	$K_3[Fe(CN)_6]$	$(VO_2)_2SO_4$	The solution was heated at 105°C for 5 h.	1.00	23.0	8
BFFC	Corn stover alkaline lignin	$K_3[Fe(CN)_6]$	$(VO_2)_2SO_4$	The solution was heated at 120°C for 30 min.	1.15	139.9	9
LFFC	**Enzymatic hydrolysis lignin**	**None**	**$(VO_2)_2SO_4$**	**None**	**1.67**	**159.9**	**This work**

Supplementary References

1. H. Yang, Y. Bai, D. Ouyang, F. Wang, D. Liu and X. Zhao, *J. Energy Chem.*, 2021, **58**, 133-146.
2. D. Ouyang, Y. Han, F. Wang and X. Zhao, *Bioresour. Technol.*, 2022, **344**, 126189.
3. C. She, X. Zu, Z. Yang, L. Chen, Z. Xie, H. Yang, D. Yang, G. Yi, Y. Qin and X. Lin, *Chem. Eng. J.*, 2023, **452**, 139266.
4. W. Liu, W. Mu, M. Liu, X. Zhang, H. Cai and Y. Deng, *Nat. Commun.*, 2014, **5**, 3208.
5. W. Liu, Y. Gong, W. Wu, W. Yang, C. Liu, Y. Deng and Z. s. Chao, *ChemSusChem*, 2018, **11**, 2229-2238.
6. J. Gong, W. Liu, X. Du, C. Liu, Z. Zhang, F. Sun, L. Yang, D. Xu, H. Guo and Y. Deng, *ChemSusChem*, 2017, **10**, 506-513.
7. Y.-A. Chen, H. Yang, D. Ouyang, T. Liu, D. Liu and X. Zhao, *Appl. Catal., B*, 2020, **265**, 118578.
8. D. Ouyang, F. Wang, H. Yang and X. Zhao, *Chem. Eng. J.*, 2021, **420**, 129716.
9. F. Wang, D. Ouyang, B. Li, T. Liu and X. Zhao, *Energy Convers. Manage.*, 2022, **258**, 115552.