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Supporting information

Synthesis of Fluorinated Biomimetic Hydrophobic Gas Diffusion Cathode for Catalytic Hydrogen Peroxide Qi Yu^{a*}, Zhexiu Liu^a, Jiefei Li^{a*}

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Methods

GF Electrode Modification and Experiment:

Specifically, a quantitative amount of ACET and a certain proportion of PTFE (60%) were dispersed in a mixture of 75 mL deionized water and 25 mL ethanol to prepare the impregnation solution, which was ultrasonically mixed for 30 minutes. The GF (graphite felt), previously degreased by ultrasonication in acetone for 1 hour, was cut into circular pieces with a diameter of 75 mm and placed at the bottom of a sintered glass funnel (P100 type, inner diameter 75 mm). The impregnation solution was filtered under either atmospheric or reduced pressure until the GF was fully saturated. The filtrate was completely removed, and the GF was taken out and placed in an oven. **Atmospheric Pressure Filtration**: The GF was placed in a beaker, and the impregnation solution was poured into it. After the GF was immersed in the solution, it was ultrasonically treated for 0.5 hours.

Reduced Pressure Filtration: The 75 mm GF was placed on filter paper in the sintered glass funnel, and a 5% solid-content impregnation solution was evenly poured into it. The funnel opening was sealed, and a circulating water vacuum pump was turned on to filter until no filtrate remained. The surface of the GF was observed for any excess carbon slurry-like deposits. If none were present, more impregnation solution was added, and the filtration process was repeated until excess carbon slurry-like deposits appeared. The GF was then flipped, and the same process was repeated to remove excess carbon slurry-like deposits. The GF was then placed in a concentrated impregnation solution with 80% solid content and ultrasonically agitated for 30 minutes to ensure uniform loading. After removal, the surface carbon slurry-like deposits were cleaned off, and the GF was dried. It was then transferred to a carbonization furnace and calcined at 360°C for 60 minutes. After cooling to room temperature, it was used as the cathode electrode.

To investigate the effects of PTFE and ACET on GF modification, the prepared modified GF and unmodified GF were cut into sizes of 1×1 cm (for electrochemical performance testing) or 3×4 cm (for H₂O₂ production testing). To distinguish between the blank, atmospheric pressure, and reduced pressure filtration-modified GF electrodes, they were labeled as BGF, APGF, and VPGF, respectively. The reactor was a single-chamber electrolytic cell, where the GF served as the cathode, and a platinum sheet was used as the counter electrode. The electrodes were arranged parallel to each other with a spacing of 2 cm, and oxygen was supplied in the middle. The electrochemical process was carried out by constant-current charging. The electrolytic cell was adjusted to pH=3 using H₂SO₄, and 50 mL of 0.5 M Na₂SO₄ was used as the electrolyte. At regular intervals, solution samples were taken from the electrolytic cell, and the H₂O₂ concentration was detected using the titanium sulfate spectrophotometric method. All analytical results were measured multiple times and averaged.

Electrochemical Characterization: 5 mg of catalyst powder was suspended in a mixed solvent containing 450 μL of water, 150 μL of ethanol, and 30 μL of 5 wt% Nafion. The mixture was ultrasonicated for 1 hour to form a homogeneous dispersion. The dispersed solution was then coated onto a rotating ring-disk electrode (RRDE) to form a uniform catalyst layer. After natural drying, the dried electrode, a calomel reference electrode, and a graphite rod counter electrode were used to construct a three-electrode system. Prior to each cyclic voltammetry (CV) test, the electrolyte (0.5 M Na₂SO₄ and 0.1 M HClO₄) was pre-saturated with pure O₂ by purging for 30 minutes to ensure oxygen saturation. Throughout the experiment, oxygen was continuously purged into the electrolyte. The oxygen reduction reaction (ORR) activity of the catalyst was investigated through CV measurements. Linear sweep voltammetry (LSV) experiments were conducted at different rotation speeds (400, 900, 1600, and 2500 rpm) within a potential range of -0.2 to 1.0 V.



Fig. S1 SEM image of the electrode a) VPGF, b) APGF ; electrode and water contact Angle c) VPGF, i) APGF .



Fig.S2 Raman spectra of different mixing ratios of PTFE / ACET: a)4%, b)6%, c)8%, d)10%, e)12%, f)Defect Density diagram



Fig.S3 a)3D Plot of Current Density(red), Contact Angle(blue), and Defect Density(purple), b)Potentials and maximum current density corresponding to different mixing ratios of PTFE / ACET



Fig. S4 LSV curves of PTFE in ACTE for different molar percentages of 4, 6, 8, 10 and 12 mol% coated glassy carbon rotating disc electrodes in O2

saturated 0.1 M $HClO_4$ solution at 400, 900, 1600 and 2500 rpm for all above tests without iR compensation.

Table S 1 (a) Calculated electron transfer coefficient data table for PTFE in ACTE 12% (mol)

Current densities(A) at differen	t voltages(V) an	nd electrode rotation	al sneeds(rnm)
Current achisteres	i i at uniti th	t fortagest f an		ai specus(i pm)

	Voltage	-0.8	-0.83	-0.865	-0.88	-0.9
rpm						
400		0.000096	0.000105	0.000114	0.00012	0.000128
900		0.000127	0.000136	0.000147	0.000153	0.00016
1600		0.000164	0.000174	0.000188	0.000194	0.000205
2500		0.000195	0.000206	0.000221	0.000229	0.000242
Fitted the tree	nd line equation	and calculated the electror	ı transfer number			
Liner						
regession		Y=56.951x+1.7314	Y= 50.18x+1.8933	Y=45.723x+1.8204	Y=42.532x+1.8798	Y=39.479x+1.8531
equation						
R ²		0.9935	0.9905	0.9902	0.9879	0.9803
Number of						
electron		2.43	2.76	3.03	3.25	3.51
transfers						

Table S 1(b) Calculated electron transfer coefficient data table for PTFE in ACTE 4% (mol)

Current densities(A) at different voltages(V) and electrode rotational speeds(rpm)

	Voltage	-0.99	-0.992	-0.993	-0.994	-0.995		
rpm								
400		0.000136	0.000142	0.000146	0.000153	0.000161		
900		0.000195	0.000195	0.000196	0.000196	0.000196		
1600		0.000273	0.000275	0.000275	0.000276	0.000276		
2500		0.000314	0.000314	0.000316	0.000316	0.000316		
Eited the trand live countion and coloulated the choice transfer number								

Fitted the trend line equation and calculated the electron transfer number

Liner					
regession	Y=45.977x+0.2727	Y=42.624x+0.521	Y=40.599x+0.6619	Y=37.156x+0.9217	Y=33.527x+1.2004
equation					
\mathbb{R}^2	0.9956	0.9908	0.9879	0.9755	0.9539
N					
Number of					
electron	3.01	3.25	3.41	3.73	4.13
transfers					

Table S 1(c) Calculated electron transfer coefficient data table for PTFE in ACTE 6% (mol)

Current densities(A) at different voltages(V) and electrode rotational speeds(rpm)								
	Voltage	-0.61	-0.78	-0.96	-0.1	-0.64		
rpm								
400		0.0000404	0.000112	0.00012	0.00013	0.0000713		
900		0.0000369	0.000139	0.000161	0.000179	0.0000592		
1600		0.0000468	0.000192	0.000206	0.000222	0.000087		
2500		0.0000502	0.000228	0.000247	0.000263	0.0000945		

Fitted the trend line equ	ation and calculated the elect	ron transfer number			
Liner regession	Y=53.198x+18.01	Y=49.315x+1.5388	Y=46.003x+1.2998	Y=41.755x+1.2556	Y=39.363x+9.3447
equation					
\mathbb{R}^2	0.4424	0.9645	0.9958	0.9997	0.3191
Number of					
electron transfers	2.6	2.81	3.01	3.32	3.52

Current dens	ities(A) at diff	erent voltages(V) and elect	rode rotational speeds(rpi	n)		
	Voltage	-0.571	-0.575	-0.83	-0.95	-1
rpm						
400		0.0000209	0.000022	0.000103	0.000115	0.000127
900		0.0000209	0.0000217	0.000128	0.000144	0.000164
1600		0.0000226	0.0000237	0.000164	0.000184	0.000205
2500		0.0000234	0.0000244	0.000177	0.000201	0.000226
Fitted the tree	nd line equatio	on and calculated the electr	on transfer number			
Liner						
regession		Y=54.421x+40.272	Y=48.586x+38.861	Y=45.063x+2.8483	Y=41.077x+2.4389	Y=37.843x+2.065
equation						
R ²		0.7298	0.6358	0.9835	0.9864	0.9955
Number of						
electron		2.54	2.85	3.07	3.37	3.66
transfers						

Volta	ge -0.509	-0.7	-0.81	-0.82	-0.85
rpm					
400	0.0000341	0.00012	0.000138	0.000144	0.00015
900	0.0000334	0.000155	0.000198	0.000199	0.000211
1600	0.0000295	0.000202	0.000244	0.000246	0.000253
2500	0.0000301	0.000243	0.000298	0.000301	0.000308
Fitted the trend line	equation and calculated the e	lectron transfer number			
Liner					
regession	Y=-49.089x+36.46	5 Y=45.264x+1.4739	Y=41.514x+0.8208	Y=38.52x+1.0192	Y=36.259x+1.055

equation					
R ²	0.7538	0.9862	0.9990	0.9982	0.9978
Number of					
electron	2.82	3.06	3.33	3.59	3.82
transfers					



Fig. S5 K-L plots of electron transfer (Koutecky-Levich plots of PTFE in ACTE at different molar percentages for different doping amounts of 4, 6, 8, 10, 12 mol% using Fig. S4.

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Catalystx loading capacity	Rs	Ret	Mathematical equation	Degree of fit
5%	0.665	1.8075	y = 0.8894x - 3.7907	$R^2 = 0.999$
8.5%	0.487	1.7735	y = 1.0349x - 3.3505	$R^2 = 0.9988$
10%	0.513	1.5835	y = 0.7458x - 2.4599	$R^2 = 0.9992$
12.5	0.531	2.5810	y = 0.8908x - 3.0264	$R^2 = 0.9931$

Table S3 ariation of hydrogen peroxide yield with current density

Hydrogen peroxide generation(mg L-1) at different time (min) and current density (mA cm-2)

Current Density/mA cm⁻²

Time/min	30mA cm-2	40mA cm ⁻²	50mA cm ⁻²	60mA cm ⁻²
0	0	0	0	0
10	213.234	441.48	733.216	713.621
20	426.608	700.13	1182.24	1126.282
30	632.954	850.447	1497.712	1414.075
40	803.04	991.952	1708.992	1628.357
50	977.242	1124.929	1833.328	1796.374
60	1128.736	1188.98	1912.32	1926.752
70	1214.458	1230.814	1910.576	1990.117
80	1216.46	1261.338	1909.76	1979.42
90	1172.584	1218.178	1907.792	1963.84

Table S4 Relationship between hydrogen peroxide production and oxygen fluxes

Hydrogen peroxide generation (mg L¹) at different times (min) and oxygen fluxes (mL/min)

	xygen fluxes (mL/min)					
Time/min	0mL/min	30mL/min	60mL/min	100mL/min	130mL/min	
0	0	0	0	0	0	
10	206.8	362.82	448	916.52	687.3	
20	376.12	729.6	816.74	1477.8	1111.6	
30	544.24	984.18	1146.52	1872.14	1512.68	
40	675	1226.8	1474.8	2136.24	1866 4	
50	910.2	1207.4	170(20	2201.66	2120.0	
50	810.2	138/.4	1/06.28	2291.66	2138.9	
60	931.4	1528.76	1933.42	2390.4	2272.24	
70	1039.26	1573.86	2110.78	2388.22	2327.88	
80	1088.76	1635.2	2159.76	2387.2	2350.66	
90	1126.62	1649.24	2190.06	2384.74	2378.74	

 $Table \ S5 \ Comparison \ of \ hydrogen \ peroxide \ production \ in \ this \ work \ with \ relevant \ literature$

Ref	Current density (mA cm ⁻²)	rH ₂ O ₂ (mg h ⁻¹ cm ⁻²)
[This Work]	50	46.21
CF - X ^[5]	5.882	39.41
FPC ^[14]	84	23.1
gc-GF ^[17]	6.7	4.44
GF/ACET/PT ^[19]	100	5
GF/CNTs-PTFE ^[29]	2.56	7.741
GF/NPC ^[30]	12.5	0.74
GF/ACET-PTFE ^[31]	50	35.96
GF-EA ^[32]	17.6	13.79
O-CNT ^[33]	8	0.97
GF-EO ^[34]	100	4.16
CB-PTFE ^[35]	50	23.46
GF-EP ^[36]	100	8.84
MWCNTs-CB-GF ^[37]	12	15.45



Figure S6 (a)Half circle flattening phenomenon of EIS spectra under different loads .(b-d)PTFE accounted for 8% of ACTE, and the mixture load accounted for 10% of the quality of graphite felt.(b)20-segment CV.(c) 400-segment CV.(d)The ratio of hydrophobic electrode and the ratio and load of PTFE in ACET

Table.S6 Contact Angle of GF and H₂O₂ Production After 50 Minutes and 100 Hours in Seven Parallel Experiments

	CA(°)	50min (mg L ⁻¹)	After 100h (mg L-1)
GF1	117.84	500	950
GF2	124.55	1000	1500
GF3	126.43	1250	1750
GF4	138.65	1775.69	2060.58
GF5	141.62	2000	2109.43
GF6	143.11	2130.58	2198.76
GF7	146.59	2350.66	2398.74