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Supporting Information

Constructing highly durable reversal-tolerant anodes via integrating high-

surface-area Ti_4O_7 supported Pt and $Ir@IrO_x$ for proton exchange membrane

fuel cells

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Figure S1. XRD patterns of the reduction of TiO₂@ PEG under different conditions.



Figure S2. Polarization curves of commercial Pt/C anode with different anode Pt loadings. Cell temperature 80°C, RH 100%, back pressure 100 kPa, stoichiometry flows (1.5/2.5).



Figure S3. Reversal tolerance test of MEAs with commercial Pt/C, 40% Pt/Ti₄O_{7,} and 50% Pt/Ti₄O₇ anodes, respectively.



Figure S4. Electrical conductivity of XC-72R, $Ti_4O_{7,}$ and TiO_2 under the pressure from 2 MPa to 30 MPa.



Figure S5. Atomic fraction of Ti and O elements analyzed by EDS mapping.



Figure S6. TEM images of 40% Pt/Ti₄O₇.



Figure S7. HAADF images of 40% Pt/Ti_4O_7 and the corresponding EDS mapping of Ti, O, and Pt elements.



Figure S8. XRD pattern of 50% Ir@IrOx/C.



Figure S9. TEM image of Ir@IrOx/Pt/Ti₄O₇.



Figure S10. XPS Ir 4f spectra of Ir@IrOx/Pt/C.



Figure S11. H₂/air polarization curves of (a) $Pt/C + IrO_2$ and $Pt/Ti_4O_7 + IrO_2$, (b) Ir@IrOx/Pt/C and Ir@IrOx/Pt/Ti₄O₇ RTAs under fixed flows.



Figure S12. EIS test results of $Pt/C + IrO_2$ and $Pt/Ti_4O_7 + IrO_2$ anodes before and after reversal test.



Figure S13. EIS test results of Ir@IrOx/Pt/C and Ir@IrOx/Pt/Ti₄O₇ anodes before and after reversal test.



Figure S14. TEM images of $Pt/C + IrO_2$ anode catalyst after the reversal test.



Figure S15. EDS mapping of $Pt/Ti_4O_7 + IrO_2$ anode catalyst after the reversal test.

Model development

When the reversible voltage exceeds 0.207 V, the carbon support becomes thermodynamically unstable and is susceptible to oxidation into carbon dioxide (CO₂). This process results in platinum being left unsupported and rendered inactive. Additionally, the loss of support leads to the agglomeration of platinum particles into larger entities, dissolution into the ionomer, or their complete removal from the system^[1].

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

In the experimental tests, carbon corrosion was quantified by measuring the CO₂ content in the exhaust gas, making CO₂ a crucial indicator for evaluating reversal performance^[2]. Given the costly and time-intensive nature of experimental approaches, numerical modeling serves as an efficient method to investigate carbon corrosion mechanisms. Consequently, a time-dependent, two-dimensional agglomerate model has been developed to enhance our understanding of carbon particle corrosion under hydrogen-starved conditions. Contrasted with alternative catalyst layer models, such as the macro-homogeneous model and the thin-film model, the agglomerate model offers a more accurate approximation for representing the catalyst layer^[3]. Within this model, the catalyst layer is conceptualized as a homogeneous matrix composed of catalyst agglomerates, each encircled by gas pores. These agglomerates are treated as uniform mixtures of the catalyst, polymer electrolytes, and void spaces.^[4], while the ionomer film thickness is set at 80 nm^[5], as depicted in Figure S16

1) Governing equations

The current density (i) resulting from the electrochemical reactions, including COR and OER, is expressed by the concentration-dependent linearized Butler-Volmer expression.

For the COR

$$i_{\text{COR}} = i_{0,\text{COR}} \left[\frac{C_{\text{CO}_2}}{C_{\text{CO}_2,\text{s}}} \exp(\frac{2F}{RT} \eta) \right]$$
(S1)

For the OER

$$i_{\text{OER}} = i_{0,\text{OER}} \left[\frac{C_{\text{H}_2\text{O}}}{C_{\text{H}_2\text{O},\text{s}}} \exp(\frac{2F}{RT} \eta) \right]$$
(S2)

where ${}^{i}_{0,\text{COR}} = 5 \cdot 10^{-9} \text{ A/m}^2$ and ${}^{i}_{0,\text{OER}} = 5 \cdot 10^{-2} \text{ A/m}^2$ is the exchange current density of COR^[6]and OER^[7], respectively. ${}^{C}_{\text{H}_2\text{O}}$ and ${}^{C}_{\text{H}_2\text{O},\text{s}}$ is H₂O concentration at local position and ionomer film surface (Figure S16), *F* is the Faraday constant, *R* is the ideal gas constant, *T* = 353 K is the temperature, and $\eta = 0.2$ V is the overpotential.

The conservation equation for the species i including H₂O and CO₂ is given by:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \left(-D_i \nabla c_i \right) = R_i$$
(S3)

where $R_i = \frac{-i}{2F}$ is the electrochemical reaction source term, D_i is the diffusion coefficient ($D_i = 4 \times 10^{-10} \text{ m}^2/\text{s}$).

The level-set interface is employed to monitor the deformation resulting from the carbon corrosion reaction. This interface is represented by the 0.5 contours of the level set variable ϕ . The ϕ variable transitions from 1 within the ionomer domain to 0 within

the solid phase region. It can, therefore, be conceptualized as the electrolyte volume fraction. The transport of the level set variable is governed by the following equation:

$$\frac{\partial \phi}{\partial t} + u \cdot \nabla \phi = \gamma \nabla \cdot (\varepsilon \nabla \phi - \phi (1 - \phi) \frac{\nabla \phi}{|\nabla \phi|})$$

where ε parameter determines the thickness of the interface, and γ parameter determines the amount of reinitialization.

2) Initial and boundary conditions

Figure S16 illustrates the boundary conditions for the agglomerate models. Initially, the concentrations of H₂O and CO₂ within all domains are set at 1 mol/m³ and 0 mol/m³, respectively. Additionally, at the ionomer film surface, the concentrations of H₂O ($^{C}_{H_2O, s}$)) and CO₂ ($^{C}_{CO_2, s}$) are also fixed at 1 mol/m³ and 0 mol/m³, respectively. Furthermore, the level set variable ϕ is set to 0 at both the Pt particle and carbon particle surfaces.



Figure S16. The geometrical structures and boundaries condition for agglomerate

model.

To gain a more comprehensive understanding of carbon corrosion phenomena, a multiphysics model was employed utilizing an aggregation model. As depicted in Figure 4f, the CO_2 concentration exhibits an increasing trend over time. For instance, the average CO_2 concentration within the ionomer domain rises from 0 at the starting time to 1.1 mol/m3 at 2 hours. Concurrently, the carbon particle undergoes gradual corrosion as time progresses. Therefore, the carbon particle surface (C surface) gradually moves away from the initial surface, and the distance between these two surfaces represents the volume loss due to COR.



Figure S17. Cyclic voltammetry (CV) curves of Ir@IrOx/Pt/C and Ir@IrOx/Pt/Ti₄O₇

before and after reversal tests.

	R _{ohm} (ohm)		R _{ct,a} (ohm)		R _{ct,c} (ohm)	
	Before	After	Before	After	Before	After
$Pt/C + IrO_2$	0.0157	0.0270	0.00477	0.00554	0.0672	0.0755
$Pt/Ti_4O_7 + IrO_2$	0.0170	0.0185	0.00417	0.00648	0.0718	0.0739
Ir@IrOx/Pt/C	0.0162	0.0267	0.00454	0.00702	0.0740	0.0869
Ir@IrOx/Pt/Ti ₄ O	0.0168	0.0173	0.00422	0.00932	0.0685	0.0720
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Table S1. Parameters obtained from the impedance fitting results.

Table S2. The comparison of anode Ir loading, first reversal time and degradation rate

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	Reversal time	Ir loading	Degradation	Reference
	(h)	$(mg_{Ir} cm^{-2})$	rate (mV h ⁻¹ @	
			1000 mA cm ⁻²)	
Cai et al.	0.97	0.05	134	[5]
Hong et al.	0.2	0.05	500	[28]
Li et al.	8.83	0.3	0.419	[19]
Zhou et al.	1.12	0.07	21.4	[29]
Mandal et al.	1.06	0.05	141	[30]
Cai et al.	0.97	0.05	123	[27]
Li et al.	0.24	0.15	250	[31]
Wang et al.	2	0.2	3	[25]
Liao et al.	2.2	0.1	68	[26]

with recently reported literature.

Wang et al.	9.3	0.1	36.2	[32]
Wang et al.	1.18	0.042	87.35	[33]
Ioroi et al.	2	0.014	9.5	[14]
Lim et al.	0.083	0.065	60	[37]
Labi et al.	0.5	0.1	120	[38]
Roh et al.	4	0.05	0	[34]
Chen et al.	5.3	0.05	0	[35]
You et al.	3	0.06	0	[36]
This work	6.12	0.05	3.43	

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