

# Probing Current Density Distribution Over Catalyst Layer at Micrometer Scale in Water Electrolyzer

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## Experimental Methods

### Materials

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (35 wt%, Sino-Platinum Metal CO., LTD);  $\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$  (35.7 wt%, Sino-Platinum Metal CO., LTD); 115 membrane (125  $\mu\text{m}$ , Dupont Company, USA); Nafion solution (D2020 from Dupont Company, USA); 2-propanol (purity  $\geq 99.9\%$ , from Sigma Aldrich), and de-ionized (DI) water (18  $\text{M}\Omega \text{ cm}$ );  $\text{ZrO}_2$  grinding balls (2mm); 60% wt Pt/C (Johnson Matthey Company, UK).

### Anode catalyst synthesis

In this study, we prepared two anode catalysts using the Adams fusion method<sup>[1]</sup>. One of the catalysts used was  $\text{RuO}_2$ , which allowed us to determine the micro-(current density) of the CL surface. The second catalyst,  $\text{IrO}_2 + \text{RuO}_2$ , with an Ir:Ru ratio of 1:4 mol%, was utilized to confirm the distribution of Ru elements.

### $\text{RuO}_2$ synthesis

To synthesize  $\text{RuO}_2$ , we initially ground the  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  precursor with an excess amount of  $\text{NaNO}_3$  until achieving a uniform mixture. Subsequently, the sample was calcined at  $450^\circ\text{C}$  for 30 minutes and thoroughly cleaned to eliminate any traces of  $\text{NaNO}_3$ . Finally, the sample was dried in an air oven at  $80^\circ\text{C}$  overnight.

### $\text{IrO}_2 + \text{RuO}_2$ (Ir:Ru = 1:4 mol%) synthesis

To prepare the  $\text{RuO}_2$  and  $\text{IrO}_2 + \text{RuO}_2$  catalysts, we dissolved the  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  and  $\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$  precursors in isopropanol, adhering to the stoichiometry, and stirred the solution for 3 hours. The resulting metal concentration in the solution was approximately 0.05M. Next, we carefully evaporated the solvent at  $80^\circ\text{C}$  using a vacuum drying oven. The resulting sample was finely ground together with an excess of  $\text{NaNO}_3$  and then transferred to a muffle furnace. In the furnace, the sample was heated to  $450^\circ\text{C}$  for 30 minutes. After allowing it to cool to

room temperature, we took the sample out of the furnace and dissolved it in DI water to remove the  $\text{NaNO}_3$ . Finally, we dried the sample overnight in an air oven at  $80^\circ\text{C}$ .

### **Catalyst-coated membrane (CCM) preparation**

To prepare the catalyst-coated membrane (CCM) with an active area of  $4\text{ cm}^2$ , we employed the decal transfer method. The cathode electrode was coated with a 60 wt% Pt/C catalyst sourced from Johnson Matthey Company, UK. As for the anode electrode, we utilized two catalysts,  $\text{RuO}_2$  and  $\text{IrO}_2+\text{RuO}_2$ , which were synthesized in-house. To prepare the catalyst ink, we combined the catalyst powder with de-ionized water ( $18\text{ M}\Omega\cdot\text{cm}$ ), Nafion solution (D2020 from Dupont Company, USA), and 2-propanol (purity  $\geq 99.9\%$ , from Sigma Aldrich). The mixture was then dispersed using a ball mill with  $\text{ZrO}_2$  grinding balls (2 mm diameter). We coated the resulting ink onto a PTFE substrate ( $50\text{ }\mu\text{m}$  thick) and subsequently transferred it onto a Nafion 115 membrane ( $125\text{ }\mu\text{m}$  thick, Dupont, US) through a hot-pressing process at  $140^\circ\text{C}$  and 2 MPa for 6 minutes. The catalyst loadings of the Catalyst Coated Membranes (CCM) were determined by weighing the PTFE material before and after the transfer process of the catalyst ink. The cathode electrode had a Pt loading of  $0.3 \pm 0.05\text{ mg cm}^{-2}$ , while the anode electrode had a noble metal (Ru or Ru+Ir) loading of  $0.5 \pm 0.05\text{ mg cm}^{-2}$ . The ionomer content in the cathode electrode was 25 wt% relative to the amount of Pt, while in the anode electrode it was 20 wt% relative to the amount of noble metal. As for the Proton Exchange Membrane (PEM) assembly, we utilized Ti mesh for the anode and carbon paper (TGP-H-060 from Toray Company, Japan) for the cathode as the Porous Transport Layers (PTL).

### **Characterization of materials**

The fresh and aged CCM samples were examined using high-resolution scanning electron microscopy (SEM) with the Zeiss GeminiSEM 500 instrument. Energy-dispersive X-ray spectroscopy (EDS) was also performed, utilizing Oxford Aztec software and an X-max 50 mm<sup>2</sup> SDD detector. The SEM and EDS analyses were conducted with a primary electron

energy of 5 keV. To investigate the elastic modulus and conductivity of the anode in MEA, we conducted Atomic Force Microscope (AFM) measurements using a multimode. Additionally, the morphology of the CCM and Ti mesh was observed using an optical microscope (OM) and a shape-measuring laser microscope (VK-X1000).

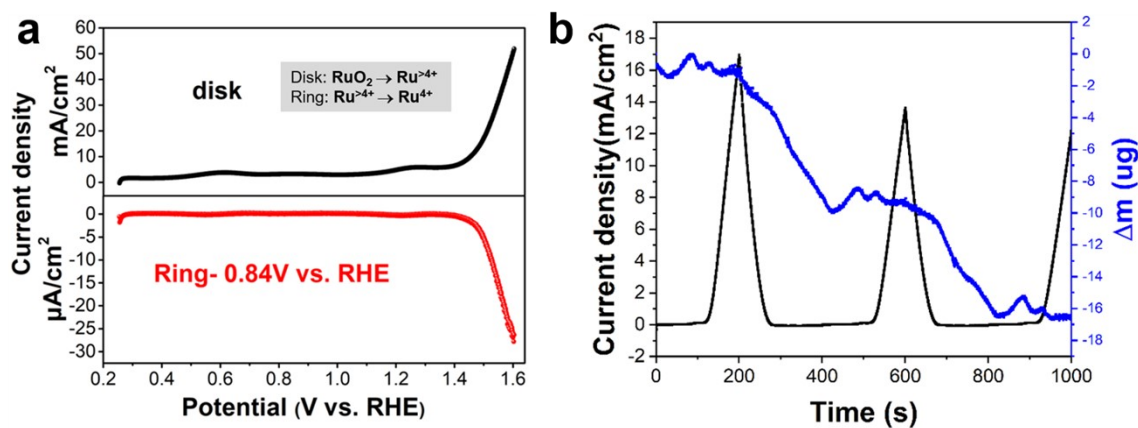
### **Electrochemical characterization**

The PEMWE was operated at a temperature of 80°C, with only DI water fed to the anode at a flow rate of 50 mL/min. Following a warm-up period, durability testing was conducted on the PEMWE using chronoamperometry at different voltage values. The aged MEA was subsequently characterized to obtain morphology and Ru distribution information until the current density decreased to 0.1 mA/cm<sup>2</sup>. The electrolyzer underwent cyclic voltammetry (CV) studies both before and after the durability test, using a scan rate of 20 mV/s<sup>-1</sup> within the voltage range of 0.3V-1.4V vs. RHE. During the measurement, H<sub>2</sub> was purged on the cathode. Electrochemical impedance spectroscopy (EIS) was conducted using a Solartron EnergyLab impedance analyzer at cell voltages of 1.2V and 1.45V, with an amplitude of 20 mV. The frequency was scanned from 100 kHz to 0.1 Hz. Prior to the test, the voltage was held at a specific level for 10 minutes to ensure that the cell reached a steady state. The EIS data were then analyzed using the EIS Analyzer software from Solartron Mobrey (UK), which is designed to fit the data and quantify the impedance of the PEMWE based on an equivalent circuit model. The morphology of the CCM and Ti mesh was characterized using an optical microscope (OM) and a shape measuring laser microscope (VK-X1000). Glassy carbon rotating disk electrode (Disk, 5 mm) and rotating ring disk electrode (Ring, 7 mm) were employed as working electrodes. The electrodes underwent a polishing process with 0.05 μm alumina powder, followed by rinsing with deionized water. Subsequently, the electrodes were sonicated separately in ethanol and deionized water. In a typical ink formulation, 2 mg of catalyst powder, 0.7 ml of deionized water, 0.3 ml of isopropanol, and 0.01 mL of 5 wt% Nafion solution were

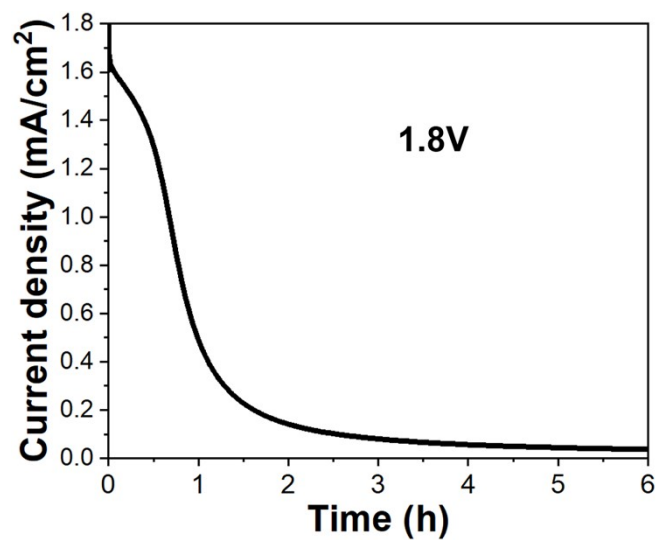
mixed together and sonicated for 1 hour prior to drop-casting. A volume of 10 microliters of the catalyst ink was then deposited onto the RDE and allowed to dry at room temperature. For the experimental setup, a graphite rod was employed as the counter electrode, while Ag/AgCl served as the reference electrode. The potentials were converted from Ag/AgCl to the reversible hydrogen electrode (RHE) using the Nernst equation ( $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.196$ ).

### **Modeling**

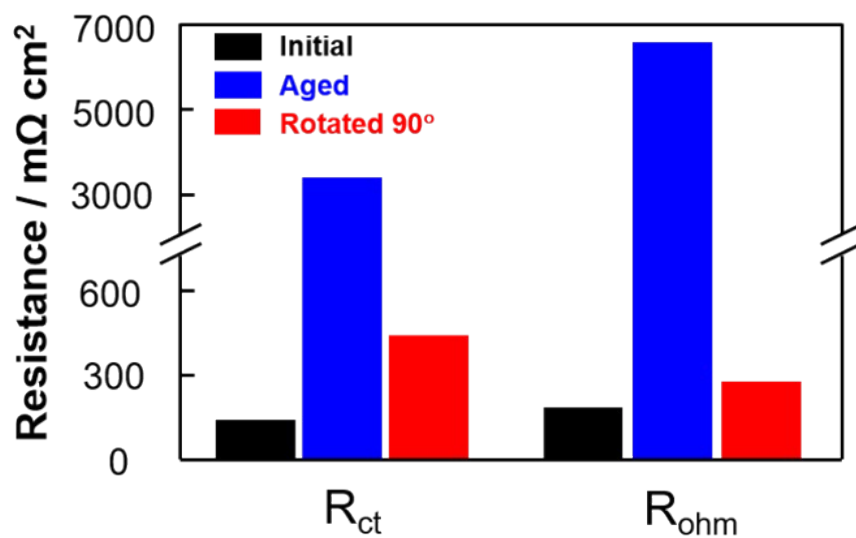
Finite element method was used for numerical simulation (COMSOL Multiphysics), both key boundary conditions and model parameters were shown in the figure. The simplified two-dimensional (2-D) model just focuses on a representative physics field characteristic of the compression zone under titanium fiber and the surrounding areas. Three physics fields were simulated, including stress field, electric field and mass concentration field. Elastoplastic analysis was used for the solid domain, bi-linear stress-strain model was adopted. The bottom boundary was fixed to avoid rigid body displacement. Time dependent mass and charge conservation were applied. The sequential coupling method was used in the simulation, which means the stress field was first simulated, the calculated volume strain was used to obtain the effective conductivity and diffusion coefficient, and then the time dependent mass concentration field and the electric field were simulated. Symmetry boundary condition was applied on the left and right vertical boundary. The titanium fiber was not explicitly simulated, a quadratic parabolic boundary load was applied instead to simulate the spatial variation of contact stress. Finer mesh was applied in the contact region (with maximum size=0.1 Tacl, minimum size=0.02 Tacl) to accurately capture the large gradient of the dependent variable in this region.



**Figure S1.** (a) Rotating ring-disk electrode voltammograms of RuO<sub>2</sub> in an air-saturated 0.5M H<sub>2</sub>SO<sub>4</sub> solution. Rotation rate: 1600 rpm. Scan rate: 10 mVs<sup>-1</sup>. The upper curve represents the disk current. The lower curves represent the corresponding ring currents at three different ring potentials. (b) Voltammetric and microgravimetric response of RuO<sub>2</sub> coated quartz crystal electrode within 0.8-1.8V in 0.5M H<sub>2</sub>SO<sub>4</sub>.

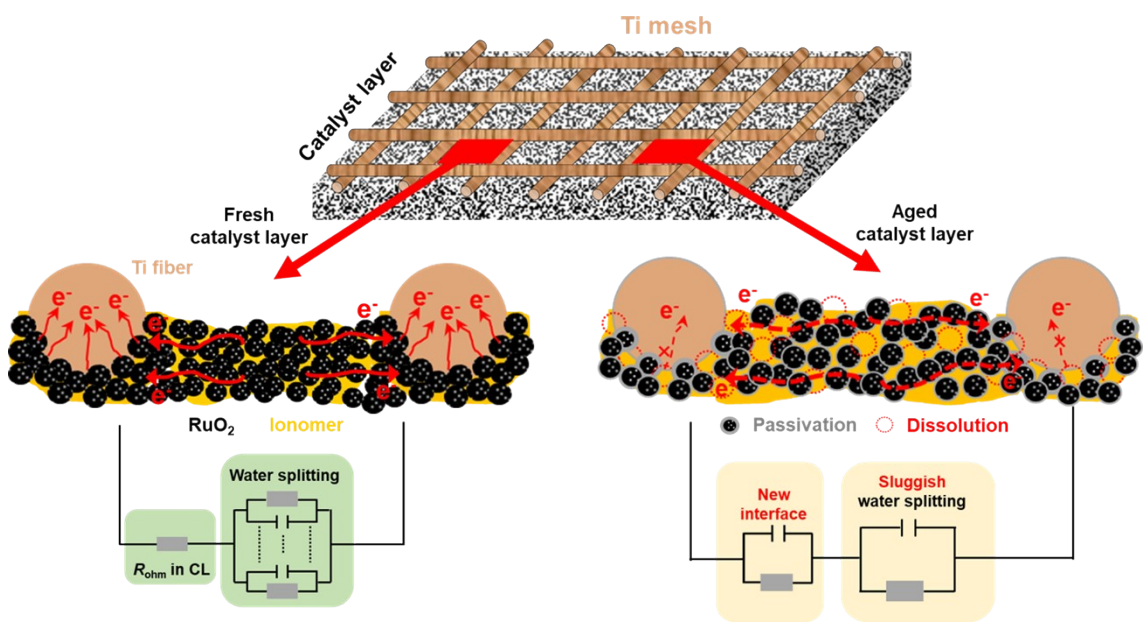


**Figure S2.** Short-term stability of PEMWE cell from beginning to 0.1 mA/cm<sup>2</sup> at 1.8V.

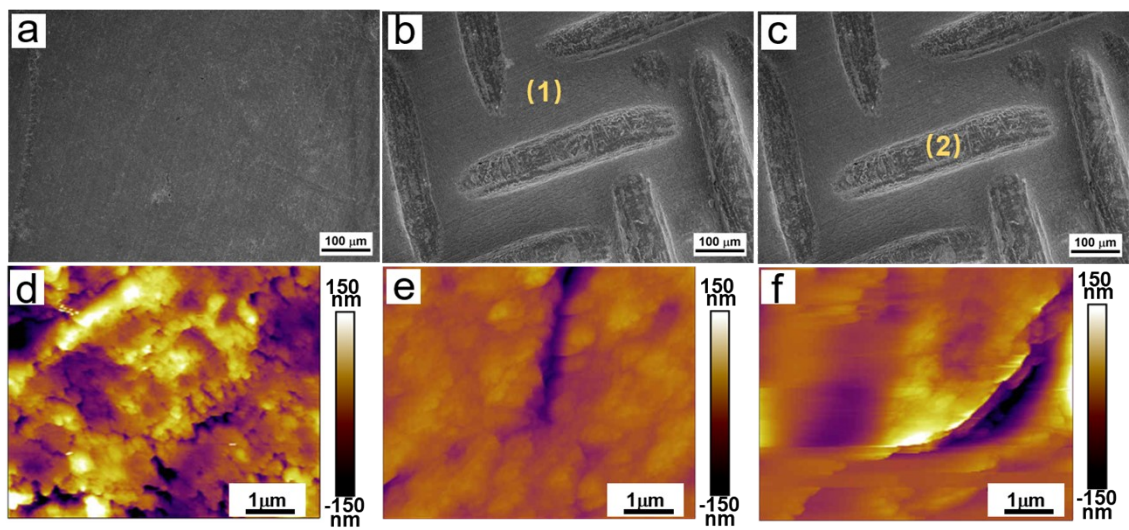


**Figure S3.** The impedance spectra of  $R_{ct}$  and  $R_{ohm}$  before and after the aged test at 1.8V.

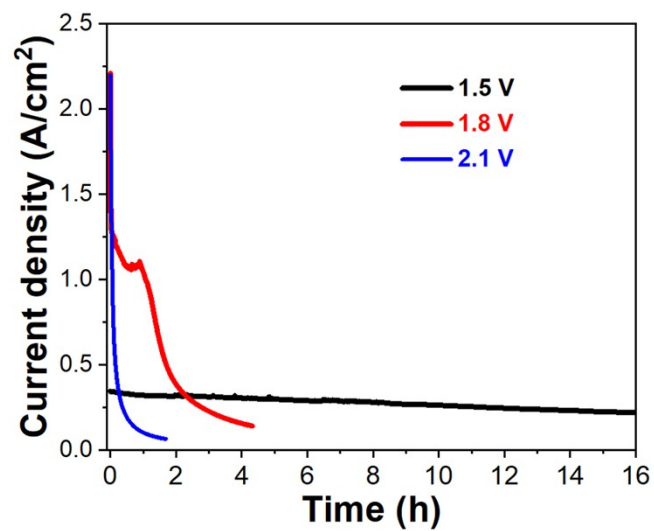




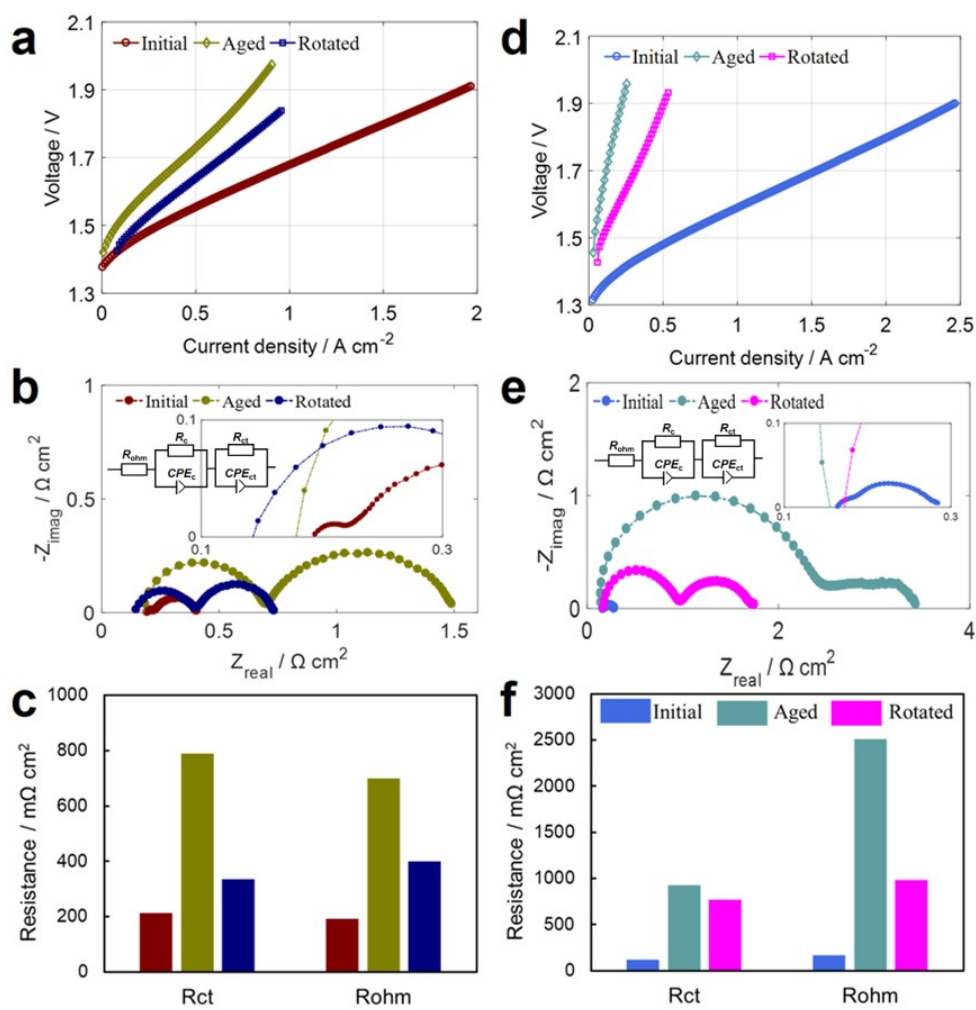
**Figure S4.** Illustration of CL inactivation before and after aging.



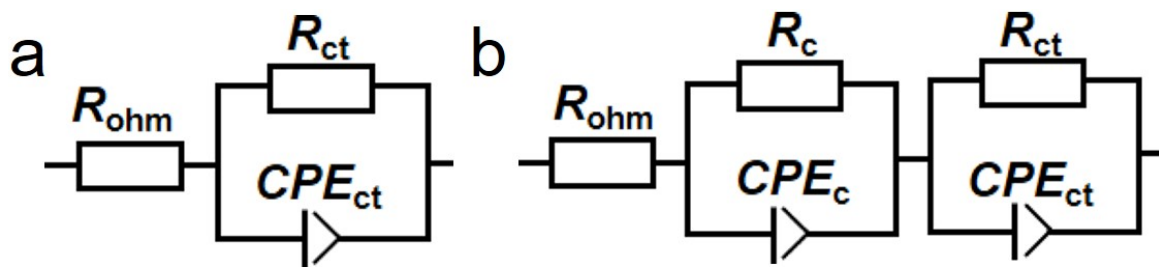
**Figure S5.** (a-c) SEM of CCM before and after aging, including under mesh and hole. (d-f) The topography of CCM by AFM measured before and after aging.



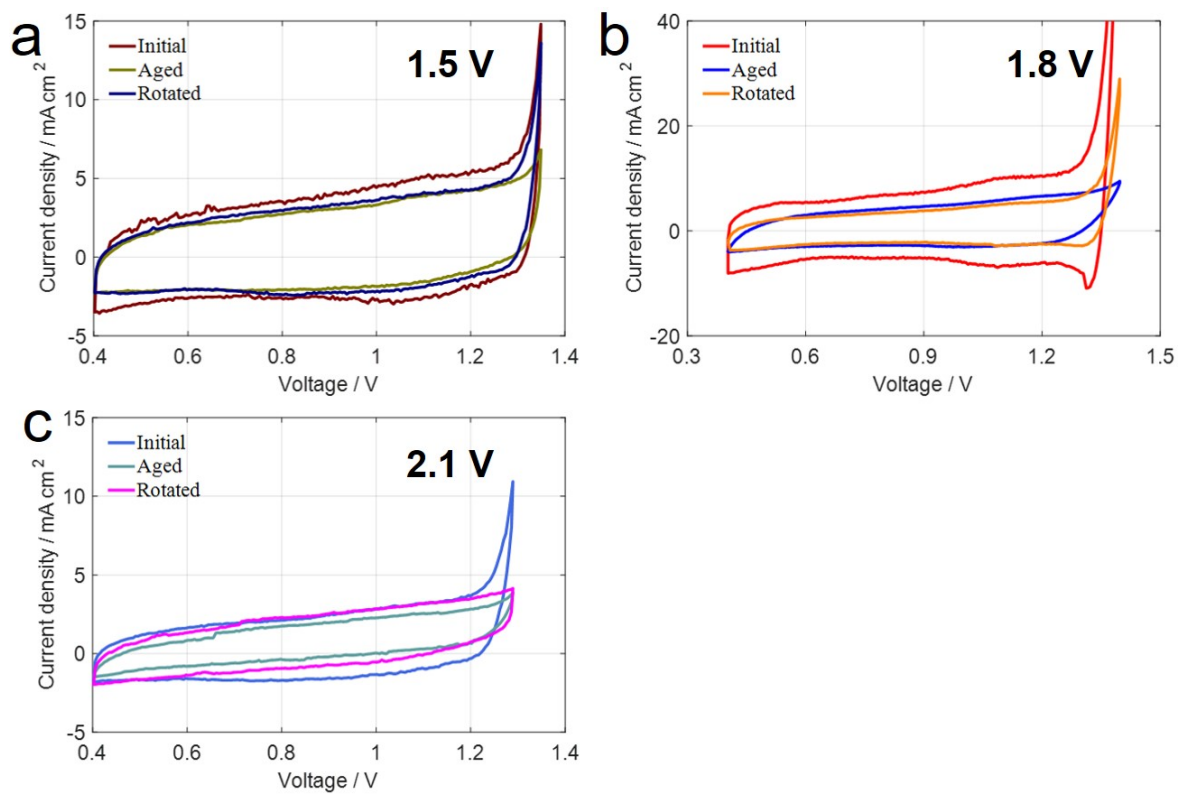
**Figure S6.** Short-term stability of PEMWE cell from beginning to 0.1mA/cm<sup>2</sup> at 1.5V, 1.8V and 2.1V.



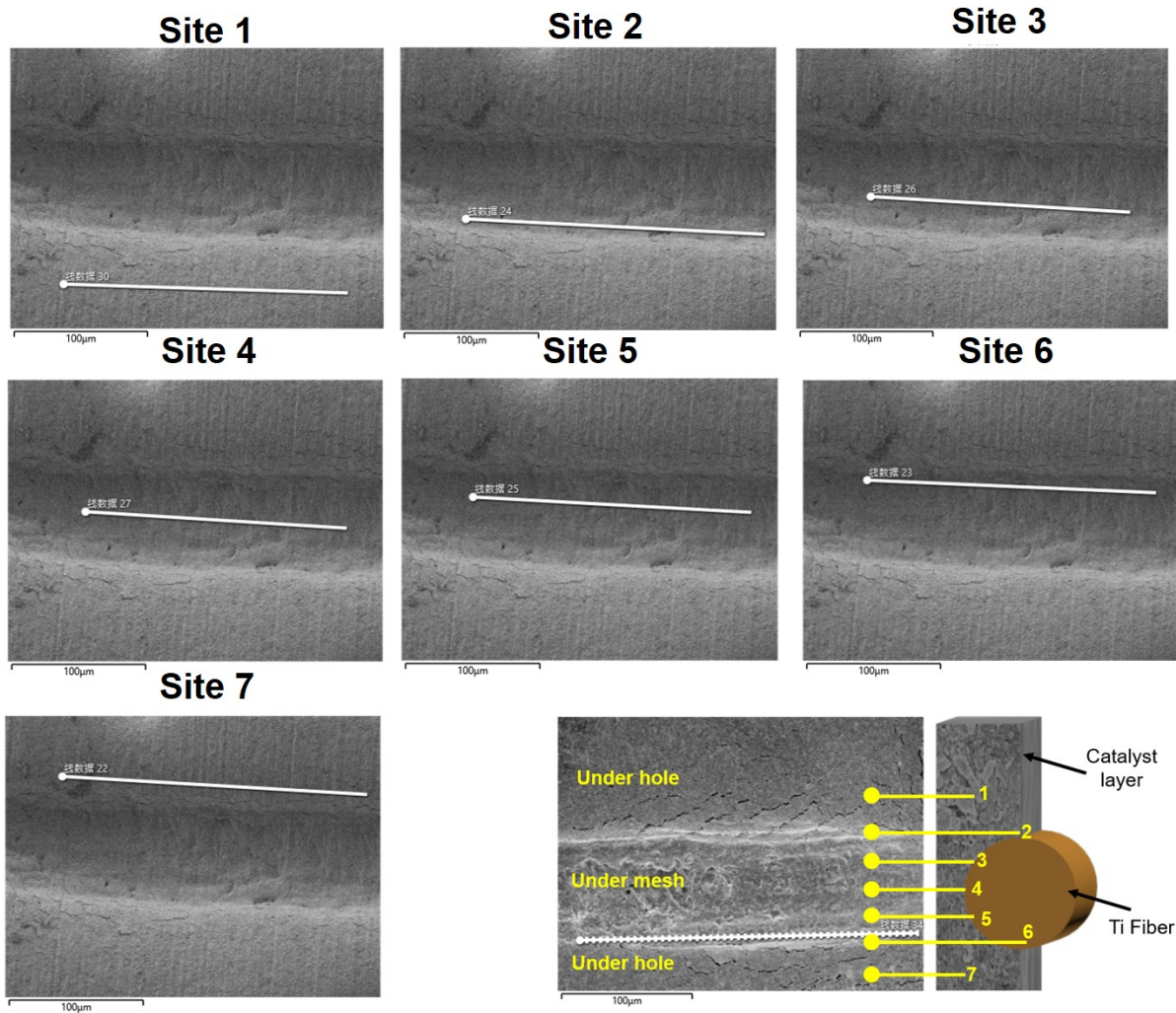
**Figure S7.** The electrochemical performance curves of RuO<sub>2</sub> as anode catalyst before and after aged tests at (a-c) 1.5V and (d-f) 2.1V.



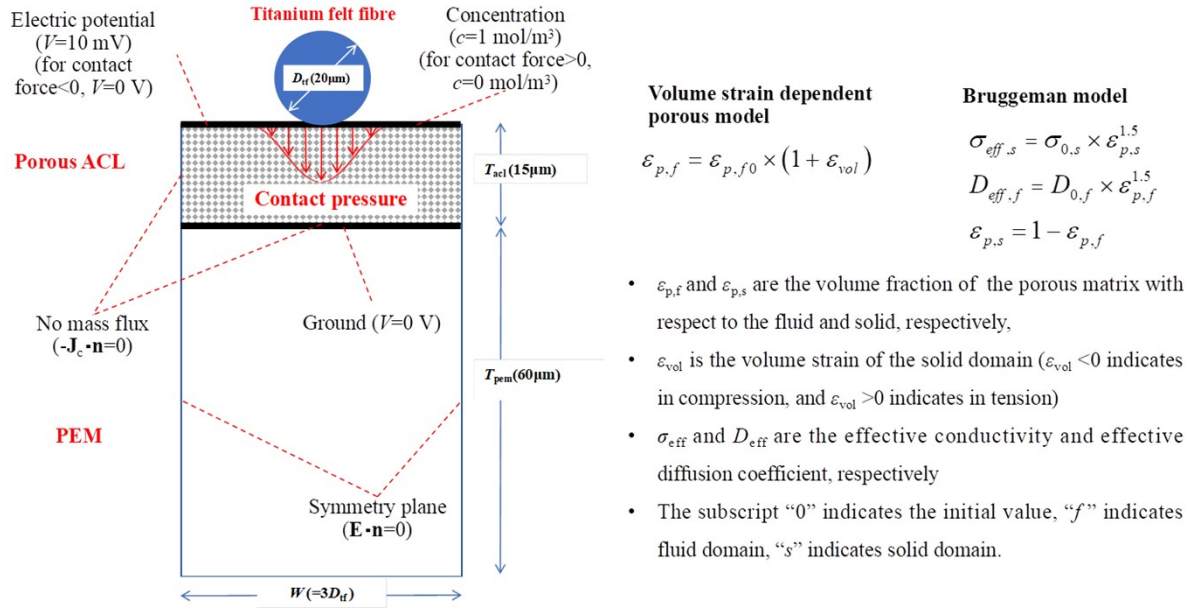
**Figure S8.** The analog circuit diagrams of impedance spectra before and after the aged test.



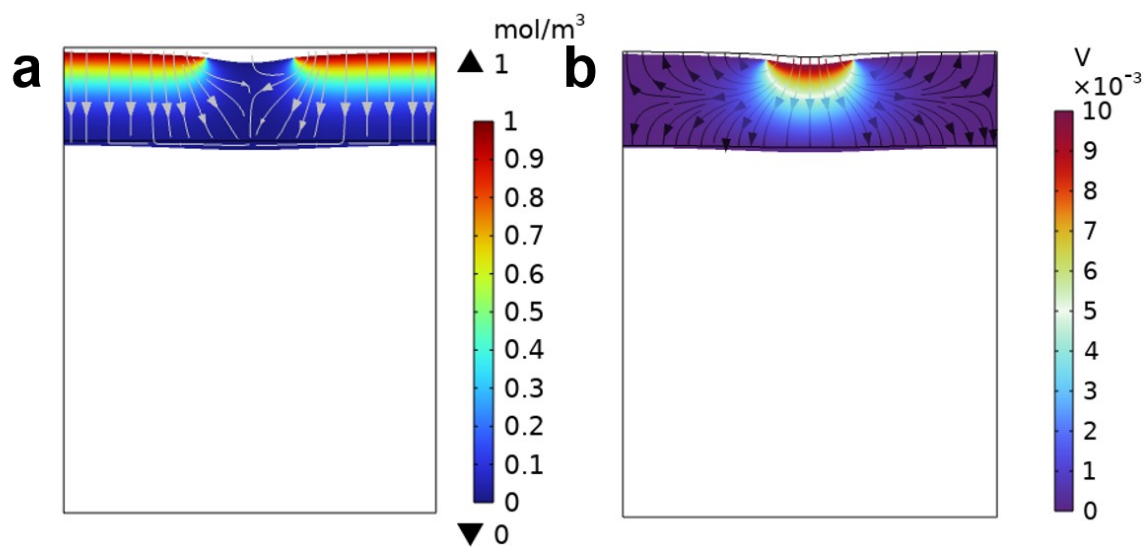
**Figure S9.** The cyclicvoltammetry of RuO<sub>2</sub> as anode catalyst before and after aged tests at (a) 1.5V, (b) 1.8V and (c) 2.1V.



**Figure S10.** SEM of the interfacial contact between catalyst layer and Ti fiber after aged test, 7 of the symmetrical positions are highlighted with yellow lines. 1 and 7, 2 and 6, 3 and 5 are symmetrical sites, respectively.



**Figure S11.** Schematic of the numerical model and the governing equation used.



**Figure S12.** (a) Mass concentration distribution of the CL surface calculated by simulation. (b) Electric potential distribution on the CL surface calculated by simulation.



Table S1. Model parameters of interface between PTL and ACL

Material	Young's modulus, $E$ (MPa)	Poisson's ratio, $\nu$	Yield stress, $\sigma_y$ (MPa)	Tangent modulus, $E_t$ (MPa)	Initial conductivity, $\sigma_0$ (S/m)	Initial diffusion coefficient, $D_0$ ( $m^2/s$ )
ACL	112	0.33	10	7.2	$1.67 \times 10^{-3}$	$1.0 \times 10^{-9}$
PEM	167	0.33	12	8.1	-	-

## Reference

1. Gupta, S. K.; Mao, Y., A Review on MoltenSalt Synthesis of Metal Oxide Nanomaterials: Status, Opportunity, and Challenge. *Progress in Materials Science* **2021**, 117.  
<https://doi.org/10.1016/j.pmatsci.2020.100734>.