

# A new insight into the chemical degradation of proton exchange membrane in water electrolyzer

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## PEMWE modelling

The major parameters covered in the modelling process is listed in table S1. The modelling was performed in COMSOL Multiphysics 6.1.

**Polarization curve modelling:** The relationship between current density and potential within PTL, GDL and PEM followed the ohm's law (formula 1 and 2):

$$\nabla \cdot i = 0$$

$$i = -\sigma \nabla \varphi$$

where  $i$  is the current density,  $\varphi$  is the potential and  $\sigma$  is the conductivity of each material. For PEM,  $\sigma_{mem}$  can be calculated via formula 3 and 4:

$$\sigma_{mem}(T) = \sigma_{303} \exp\left[\frac{1268}{303} \left(\frac{1}{303} - \frac{1}{T}\right)\right]$$

$$\sigma_{303} = 0.5139\lambda - 0.326$$

where  $T$  is the temperature,  $\sigma_{303}$  is the proton conductivity at 303 K,  $T$  is the temperature and  $\lambda$  is the water content in the membrane.

The electrochemical polarization was interpreted as Butler-Volmer equation for both cathodic and anodic reactions:

$$i_j = i_{0,j} \gamma_j \left[ \exp\left(\frac{\alpha_j z F \eta_j}{RT}\right) - \exp\left(-\frac{(1-\alpha_j) z F \eta_j}{RT}\right) \right]$$

where  $j$  is an for anodic side and  $ca$  for cathodic side,  $i_j$  is the current density,  $i_{0,j}$  is the exchange current density,  $\gamma_j$  is the active specific surface area,  $\alpha_j$  is the charge transfer coefficient,  $z$  is the number of transferred electrons,  $F$  is the Faraday's constant,  $R$  is the gas constant and  $\eta_j$  is the overpotential. Herein,  $\gamma_{an}$  and  $\gamma_{ca}$  was calculated from the measured electrochemical specific surface area of both anodic and cathodic catalysts. The exchange current density can be acquired using the following formula:

$$i_{0,j} = z F k_j T \exp\left(-\frac{A_j}{RT}\right)$$

where  $k_j$  is the rate parameter and  $A_j$  is the activation energy.

**Cathodic oxygen concentration modelling:** The gas permeation process in this model includes the dissolution of gases, diffusion and convection. The governing equation is as follow:

$$v_{H_2O} \cdot \nabla c_i = \nabla \cdot D_i \nabla c_i$$

$v_{H_2O}$  can calculated from the following equation:

$$v_{H_2O} = (-0.332 \log i + 5.59) \frac{M_{H_2O} i}{2F \rho_{H_2O}}$$

where  $M_{H_2O}$  is the molar mass of  $H_2O$  and  $\rho_{H_2O}$  is the density of  $H_2O$ .

The solubility and diffusion coefficient of both  $H_2$  and  $O_2$  can be calculated from formula 9-12:

$$S_{H_2} = \frac{1}{1.09\lambda \times \frac{M_{H_2O}}{EW} \times 10^5 \exp\left(\frac{77}{T}\right)}$$

$$S_{O_2} = 1.62 \times 10^{-6} \exp\left(\frac{603}{T}\right)$$

$$D_{H_2} = 1.23 \times 10^{-6} \exp\left(-\frac{2602}{T}\right)$$

$$D_{O_2} = 4.2 \times 10^{-6} \exp\left(-\frac{18380}{RT}\right)$$

The gas concentration can be calculated from Henry's law:

$$c_i = S_i P_i$$

where  $P_i$  is the partial pressure of specie  $i$ .

For the modelling of cathodic oxygen concentration, a steady-state calculation was performed.

The mass balance for both hydrogen and oxygen in cathodic side can be referred to as followed:

$$j_{O_2}^{perm} - j_{O_2}^{react} - j_{O_2}^g - j_{O_2}^\omega = 0$$

$$-j_{H_2}^{perm} + S_{H_2} - j_{H_2}^g - j_{H_2}^\omega = 0$$

where  $-j_i^{perm}$  is the permeation flux through the membrane of specie  $i$ ,  $j_i^{react}$  is the reaction consumption,  $j_i^g$  is the gaseous flow leaving the cell,  $j_i^\omega$  is the dissolution flux and  $S_{H_2}$  is the hydrogen generation rate in cathode side. The oxygen concentration in cathode can be calculated from:

$$x_{O_2} = \frac{j_{O_2}^g}{j_{O_2}^g + j_{H_2}^g}$$

**Membrane degradation modelling:** The cathodic  $H_2O_2$  formation rate ( $r_{ca}^{H_2O_2}$ ) was modelled as follow:

$$r_{ca}^{H_2O_2} = k_1 c_{O_2} c_{H^+}^2$$

while the anodic  $H_2O_2$  formation rate was denoted as  $r_{an}^{H_2O_2}$ , where  $k_1$  is the rate constant of reaction

1.  $c_{H^+}$  can be calculated from formula 18:

$$c_{H^+} = \frac{\rho_{mem}}{EW} = \frac{1980 + 32.4\lambda}{(1 + 0.00648\lambda)EW}$$

where  $\rho_{mem}$  is the humidity-dependent density of PEM and EW is the equivalent weight of PEM.

Further, both cathodic and anodic  $H_2O_2$  was consumed via the first step of Fenton's reaction (reaction 2) to form hydroxyl radicals, and the reaction rate was modelled as formula 19:

$$r_{HO\cdot} = k_2 c_{H_2O_2} c_{Fe^{2+}} + c_{H^+}^2$$

where  $k_2$  is the rate constant of reaction 2 and  $c_{Fe^{2+}}$  was estimated to be 10 ppm. Finally, the chemical degradation of PEM ionomer was modelled as formula 20:

$$r_{F^-} = k_3 c_{HO\cdot}$$

where  $k_3$  is the estimated rate constant of membrane degradation reaction induced by  $HO\cdot$  radicals.

The mass transfer within the PEM follows formula 21:

$$v_{H_2O} \cdot \nabla c_i = \nabla \cdot D_i \nabla c_i$$

where  $v_{H_2O}$  is the electroosmotic velocity,  $D_i$  and  $c_i$  is the diffusion coefficient and concentration of specie  $i$ ,  $i$  can be  $H_2O_2$ ,  $HO\cdot$  and  $F^-$ . The diffusion coefficient of  $F^-$  ions in Nafion 115 was approximately to be that in water, and the value is about  $1 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ .

The transfer of hydroxyl radicals was ignored due to the extremely short dwell time. For the steady-state investigation, a mass balance was written on both cathode side and anode side for  $H_2O_2$ , hydroxyl radicals and  $F^-$  ions, shown as equation 22-24, where  $j_i^{gene}$  is the generating rate of specie  $i$ ,  $j_i^{cons}$  is the consumption rate of specie  $i$  through chemical reactions,  $j_i^{perm}$  is the transfer flux through the membrane and  $j_i^{effl}$  is the effluent flux out from the cell. All the variates in equation 17-19 is inward flux, namely the value is negative when specie  $i$  is a net outflow. The final FRR can be determined by  $j_F^{effl}$  in both cathode and anode.

$$j_{H_2O_2}^{gene} + j_{H_2O_2}^{cons} + j_{H_2O_2}^{perm} + j_{H_2O_2}^{effl} = 0$$

$$j_{HO\cdot}^{gene} + j_{HO\cdot}^{cons} + j_{HO\cdot}^{effl} = 0$$

$$j_F^{gene} + j_F^{perm} + j_F^{effl} = 0$$

Table S1: Major parameters covered in the modelling process

Parameter	Symbol	Value	Reference
Thickness of anodic PTL	$t_{an}$	250 $\mu\text{m}$	/
Thickness of cathodic GDL	$t_{ca}$	250 $\mu\text{m}$	/
Thickness of PEM	$t_{mem}$	127 $\mu\text{m}$	/
Conductivity of PTL	$\sigma_{an}$	13,700 $\text{S m}^{-1}$	/
Conductivity of GDL	$\sigma_{ca}$	120 $\text{S m}^{-1}$	/
Anodic active specific surface area	$\gamma_{an}$	$1.60 \times 10^9 \text{ m}^{-1}$	/
Cathodic active specific surface area	$\gamma_{ca}$	$7.06 \times 10^7 \text{ m}^{-1}$	/
Anodic charge transfer coefficient	$\alpha_{an}$	0.65	1
Cathodic charge transfer coefficient	$\alpha_{ca}$	0.51	1
Faraday's constant	F	96,485 $\text{C mol}^{-1}$	/
Gas constant	R	8.314 $\text{J K}^{-1} \text{ mol}^{-1}$	/
Anodic activation energy	$A_{an}$	62,836 $\text{J mol}^{-1}$	1
Cathodic activation energy	$A_{ca}$	24,359 $\text{J mol}^{-1}$	1
Anodic rate parameter	$k_{an}$	$4.63 \times 10^{-3} \text{ mol K}^{-1} \text{ s}^{-1} \text{ m}^{-2}$	1
Cathodic rate parameter	$k_{ca}$	0.01 $\text{mol K}^{-1} \text{ s}^{-1} \text{ m}^{-2}$	1
Number of water molecules per sulfonate site	$\lambda$	16	2
Equivalent weight of Nafion 115	EW	1100 $\text{g mol}^{-1}$	3
Diffusion coefficient of $\text{H}_2\text{O}_2$	$D_{\text{H}_2\text{O}_2}$	$2.4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$	4
Diffusion coefficient of $\text{F}^+$ ions	$D_{\text{F}}$	$1 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$	/
$\text{Fe}^{2+}$ concentration	$c_{\text{Fe}^{2+}}$	10 ppm	/
Rate constant of cathodic $\text{H}_2\text{O}_2$ yielding	$k_1$	$4.09 \times 10^{-9} \text{ m}^6 \text{ mol}^{-2} \text{ s}^{-1}$	5
Rate constant of first step of Fenton's reaction	$k_2$	$4.18 \times 10^6 \text{ m}^9 \text{ mol}^{-3} \text{ s}^{-1}$	6
Rate constant of PEM degradation	$k_3$	$4 \times 10^6 \text{ s}^{-1}$	1,7

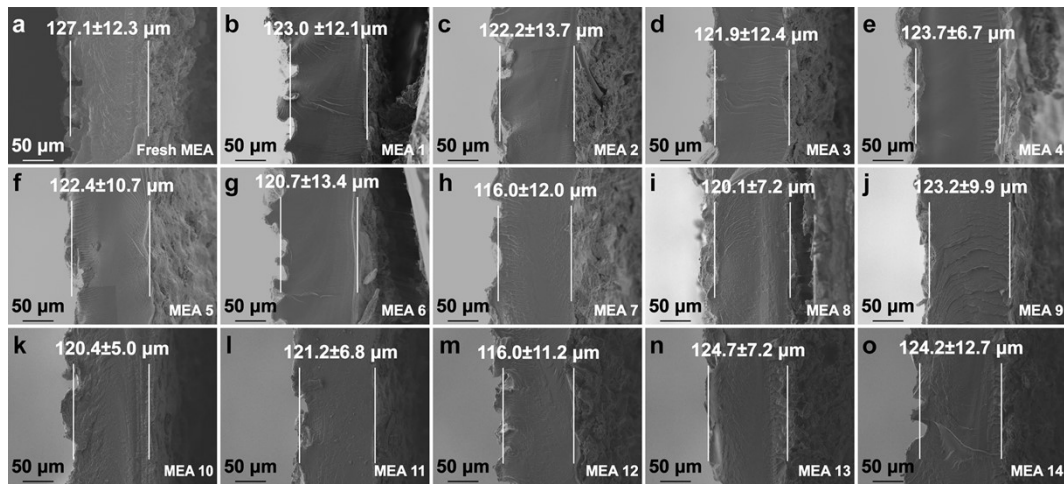


Figure S1. SEM cross-sectional image of fresh Nafion115 based MEA (a) and degraded MEAs after different testing conditions (b-o).

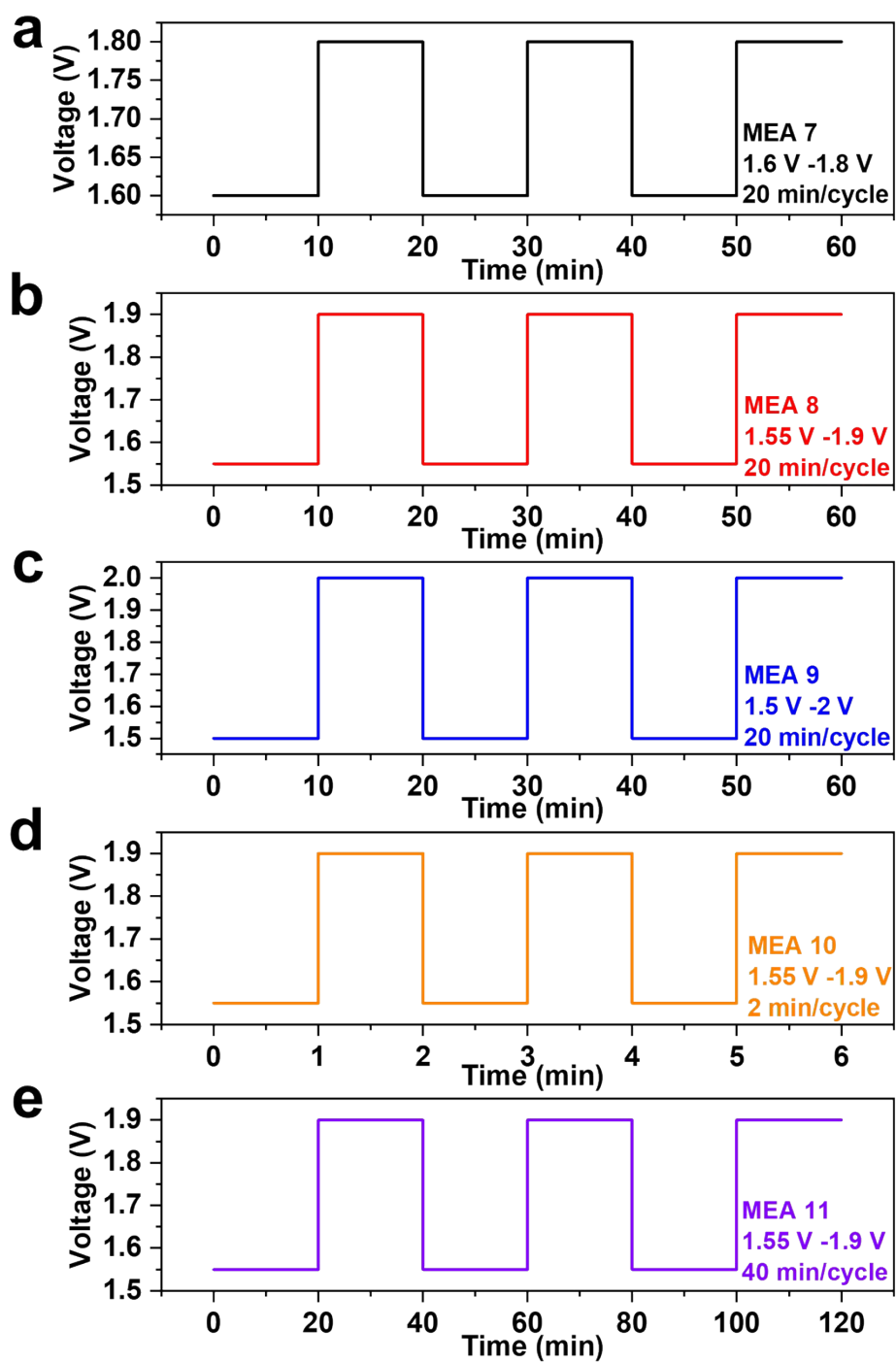


Figure S2. Power supply profile of the fluctuant voltage durability tests for MEA 7-11.

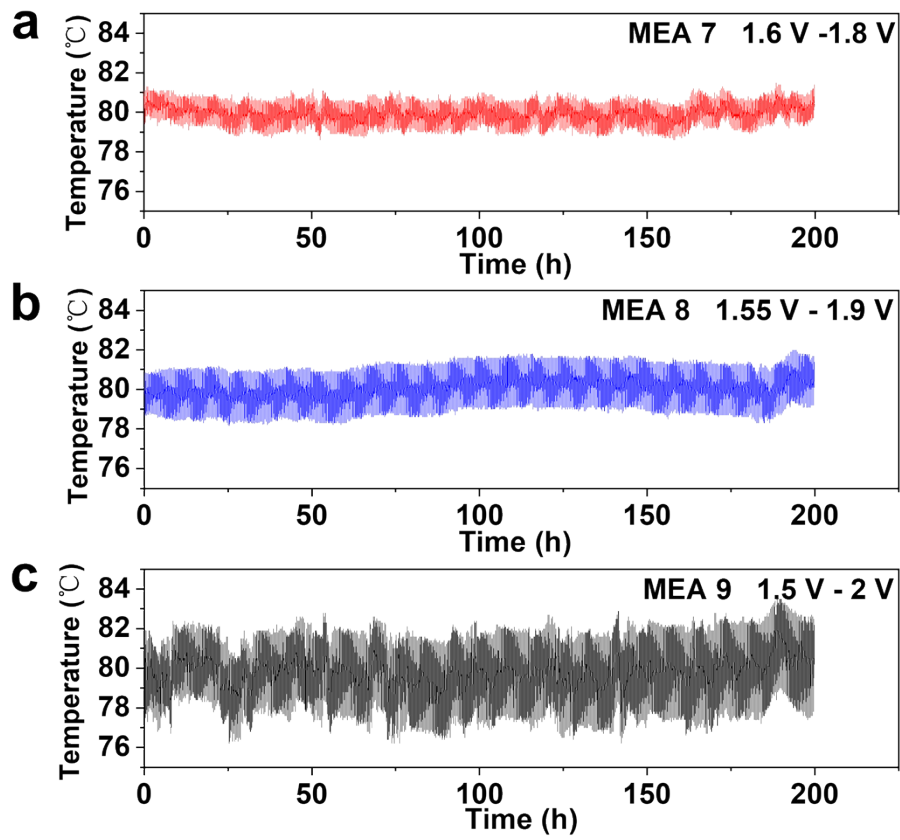


Figure S3. Temperature as a function of testing time under fluctuant voltage tests with voltage range of (a) 1.6 V - 1.8 V (MEA 7), (b) 1.55 V - 1.9 V (MEA 8), (c) 1.5 V - 2 V (MEA 9).



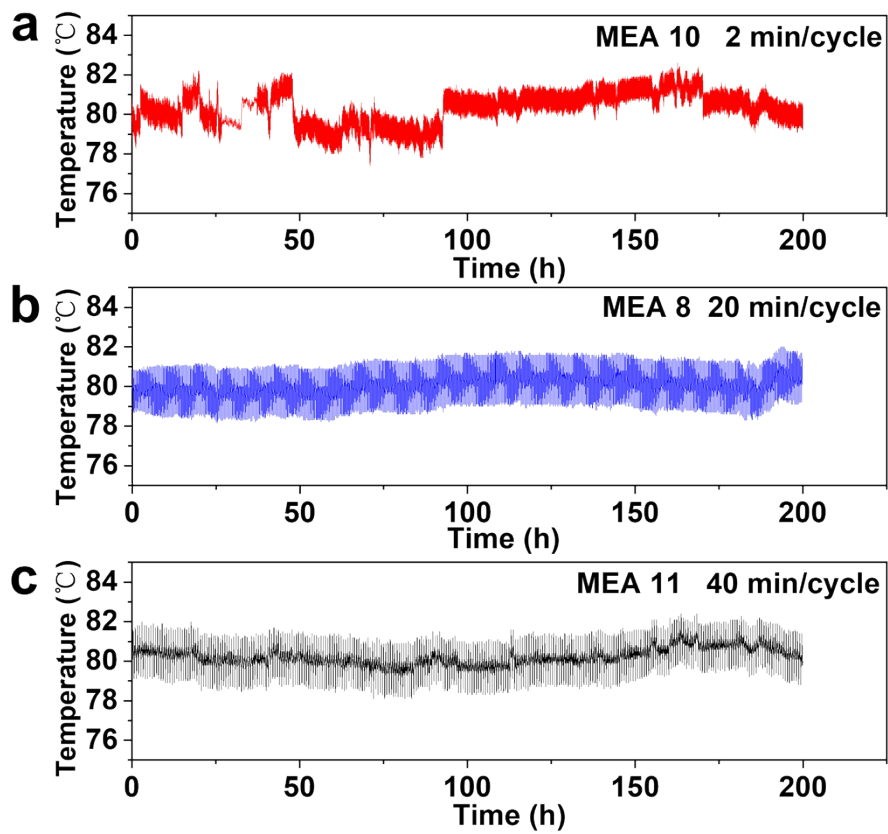


Figure S4. Temperature as a function of testing time under fluctuant voltage tests with period of (a) 2 min/cycle (MEA 10), (b) 20 min/cycle (MEA8) and (c) 40 min/cycle (MEA 11).

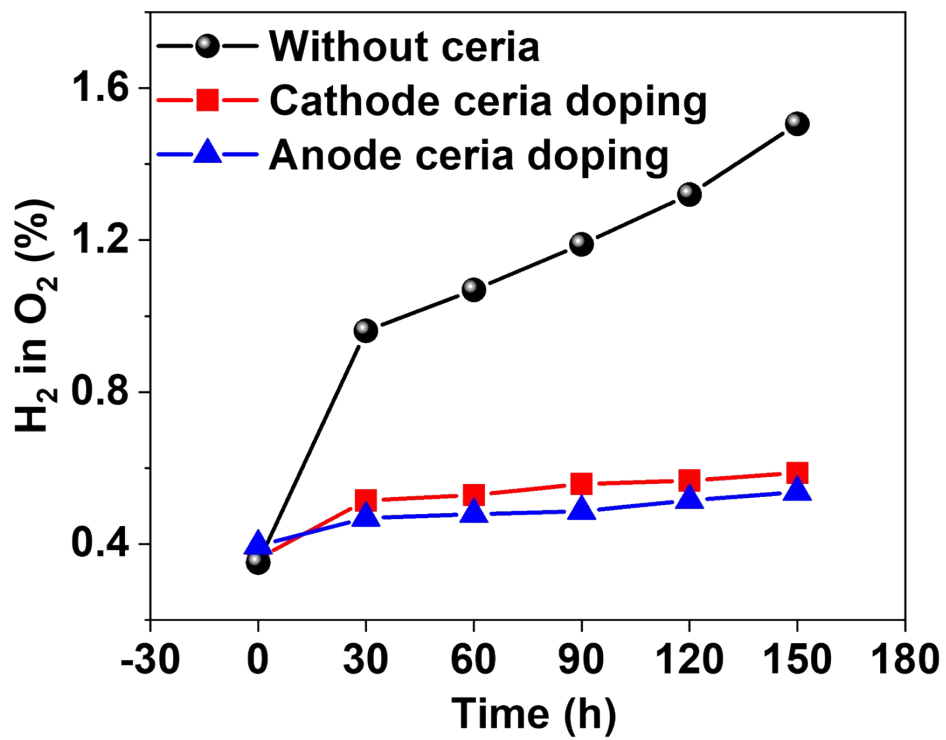


Figure S5. Anode H<sub>2</sub> concentration recorded during the 1.8 V steady state durability tests for MEA 12-14.

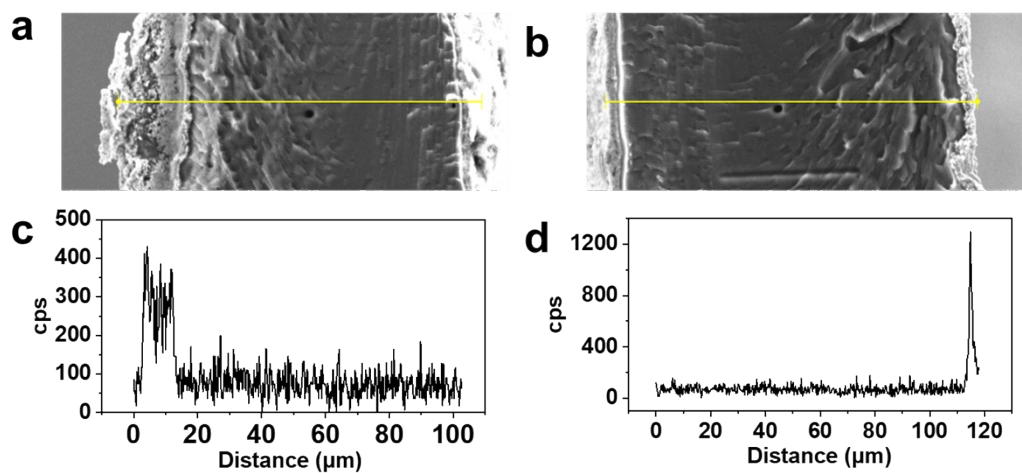


Figure S6. (a) SEM cross-sectional image and (c) EDS line scan spectrum of Ce for the cathodic ceria doped MEA after durability test; (b) SEM cross-sectional image and (d) EDS line scan spectrum of Ce for the anodic ceria doped MEA after durability test.

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