## **Supporting Information**

# Twofold Effects of Zirconium Doping into TiN on Durability and Oxygen Reduction Reactivity in Acid Environment

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#### S1. Zirconium doping level of $Ti_{1-d}Zr_dO_xN_y$ catalysts.

Ti<sub>1-d</sub>Zr<sub>d</sub>O<sub>x</sub>N<sub>y</sub> catalysts with four different *d* of 0.1, 0.2, 0.3 and 0.4 were synthesized by putting different mass of ZrCl<sub>4</sub> into a precursor dispersion. The *d* value of the catalysts evaluated using an energy dispersive X-ray spectroscopy (EDS), *d*<sub>EDS</sub>, is plotted as a function of the nominal zirconium doping level calculated from the mass of TiOSO<sub>4</sub> and ZrCl<sub>4</sub> used for the synthesis, *d*, in **Figure S1**. The *d*<sub>EDS</sub> is almost the same as *d* and the standard deviations displayed by error bars are small enough when  $d \le 0.3$ , indicating that the precursors were mixed well and did not evaporate during the pyrolysis. A large error bar is observed at d = 0.4, suggesting that some improvements are needed to prepare the precursors. Overall, it is fair to say that the *d* of Ti<sub>1-d</sub>Zr<sub>d</sub>O<sub>x</sub>N<sub>y</sub> is well controlled by simply changing the mass of ZrCl<sub>4</sub> in the precursor dispersion.



**Figure S1.** Zirconium doping level measured using an energy dispersive X-ray spectroscopy versus that calculated from the mass of TiOSO<sub>4</sub> and ZrCl<sub>4</sub> precursors ( $d_{EDS} - d$  curve of Ti<sub>1-d</sub>Zr<sub>d</sub>O<sub>x</sub>N<sub>y</sub> catalysts).

# S2. Effect of electrolyte solution on oxygen reduction reaction (ORR) activity of $Ti_{0.9}Zr_{0.1}O_xN_y$ catalyst.

It is well known that the ORR activity of platinum catalysts in 0.1 mol dm<sup>-3</sup> HClO<sub>4</sub> is higher than that in 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> because (bi)sulfates from H<sub>2</sub>SO<sub>4</sub> adsorbed on the platinum surface block the initial adsorption of O<sub>2</sub> molecules.<sup>S1</sup> Similar effect of (bi)sulfates on the ORR activity of oxide/oxynitride catalysts has not been reported and thus rotating disk electrode (RDE) voltammograms of Ti<sub>0.9</sub>Zr<sub>0.1</sub>O<sub>x</sub>N<sub>y</sub> catalyst were measured in 0.1 mol dm<sup>-3</sup> HClO<sub>4</sub> and 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> as shown in **Figure S2**. The activity is almost the same in both electrolytes indicating that the adsorption of (bi)sulfates on this catalyst is not significant.



**Figure S2.** Rotating disk electrode (RDE) voltammograms of  $Ti_{0.9}Zr_{0.1}O_xN_y$  catalyst after N<sub>2</sub> pyrolysis at 1173 K for 2 h. The scans are performed under N<sub>2</sub> and O<sub>2</sub> atmospheres using a rotation speed of 1500 rpm and a scan rate of  $-5 \text{ mV s}^{-1}$  (cathodic) in 0.1-mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 0.1-mol dm<sup>-3</sup> HClO<sub>4</sub>. The catalyst loading is constant at 0.86 mg cm<sup>-2</sup>.

#### S3. Crystal structure and morphology of Ti<sub>1-d</sub>Zr<sub>d</sub>O<sub>x</sub>N<sub>y</sub> catalysts.

The X-ray diffraction (XRD) patterns of  $Ti_{1-d}Zr_dO_xN_y$  catalysts at around TiN (2 0 0) plane are shown in **Figure S3**. The peak shifts to lower angles as *d* increases. This indicates that the lattice is expanded.

Their morphologies were investigated using field emission-scanning electron microscopy (FE-SEM) images which are shown in **Figure S4**. All the catalysts were composed of particles with less than 100 nm.



**Figure S3.** X-ray diffraction (XRD) patterns at  $2\Theta = 40-45^{\circ}$  of  $Ti_{1-d}Zr_dO_xN_y$  catalysts for four different values of *d*: (i) 0.1, (ii) 0.2, (iii) 0.3 and (iv) 0.4 after N<sub>2</sub> pyrolysis at 1173 K for 2 h.



**Figure S4.** Field emission-scanning electron microscopy (FE-SEM) images of  $Ti_{1-d}Zr_dO_xN_y$  catalysts for four different values of *d*: (i) 0.1, (ii) 0.2, (iii) 0.3 and (iv) 0.4 after N<sub>2</sub> pyrolysis at 1173 K for 2 h.

#### S4. Chemical states of $Ti_{1-d}Zr_dO_xN_y$ catalysts.

The X-ray photoelectron (XP) spectra of  $Ti_{0.8}Zr_{0.2}O_xN_y$  catalyst are shown in Figure S5. The Ti 2p and Zr 3d core levels split into Ti  $2p_{3/2}$  / Ti  $2p_{1/2}$  and Zr  $3d_{5/2}$  / Zr  $3d_{3/2}$  levels, respectively. Thus, doublets are shown in both spectra. The Ti 2p spectrum displays three pairs of doublets which are assigned to (1) TiO<sub>2</sub> phase whose Ti  $2p_{3/2}$  peak at ~ 459 eV, (2) nitrogen-doped TiO<sub>2</sub> phase at ~457 eV, and (3) TiN phase at ~455 eV. <sup>S2,S3</sup> In contrast, only one doublet is displayed in the Zr 3d spectrum whose Zr  $3d_{5/2}$  peak locates between that of Zr<sup>4+</sup> in ZrO<sub>2</sub> (183.5 eV)<sup>S4</sup> and of metallic Zr (179.0 eV),<sup>S5</sup> and can be assigned to either  $Zr^{4+}$  that is substituted for  $Ti^{4+}$  in  $TiO_2^{S4}$  or  $Zr^{4+}$  in nitrogen-doped ZrO<sub>2</sub>.<sup>S6,S7</sup> Since the peaks derived from these two different phases overlap each other, a precise deconvolution of the Zr 3d spectra is not possible. The N 1s spectrum displays four peaks and the highest one at ~401 eV is assigned to interstitial nitrogen atoms in TiO<sub>2</sub> lattice,<sup>S8</sup> while the other three ones can be from two components. The peak at ~399 eV is from both O-Ti-N bonding in nitrogen substituted TiO<sub>2</sub> lattice<sup>S9</sup> and nitrogen atoms in nitrogen-doped ZrO<sub>2</sub>,<sup>S6</sup> while that at ~397 eV is from both N-Ti-N bonding in nitrogen substituted TiO<sub>2</sub> lattice<sup>S9,S10</sup> and nitrogen atoms in ZrN.<sup>S6</sup> The lowest one at ~396 eV is from both nitrogen atoms in TiN<sup>S2</sup> and those in ZrN<sub>2</sub>.<sup>S6</sup> These overlapping peaks make the precise discussion with the deconvolution of the N 1s spectrum impossible. The O 1s spectrum is also asymmetric to display two peaks; the lower one at ~531 eV is from oxygen atoms in both TiO<sub>2</sub> and  $ZrO_2$  and the higher one at ~532 eV is from oxygen atoms in both nitrogen doped TiO<sub>2</sub> and nitrogen doped ZrO<sub>2</sub>.<sup>S6</sup> Moreover, contaminants from the XP spectrometer and air can contribute to these peaks and thus the precise discussion with the deconvolution of the O 1s spectrum is avoided.

Based on these assignments, quantitative analyses are performed only on the Ti 2p spectra before and after sputtering the surface. **Figure S6** shows Ti 2p spectra of the  $Ti_{0.8}Zr_{0.2}O_xN_y$  catalyst after five different sputtering time,  $t_s$ . The area fraction of the components (1) TiO<sub>2</sub> and (2) nitrogen-doped TiO<sub>2</sub> decreases while only that of (3) TiN increases as  $t_s$  increases, indicating that the thin surface oxide layer is removed by sputtering and the subsurface is TiN which agrees well with the results from XRD and

Raman analyses from Figure 1(a) and (b). The area fraction of the abovementioned three components,  $s_1$ ,  $s_2$  and  $s_3$  are summarized in Figure 2(II).

The XP spectra of  $Ti_{1-d}Zr_dO_xN_y$  catalysts are shown in **Figure S7**. All the Ti 2p, Zr 3d, N 1s and O 1s spectra change little as *d* increases. This indicates that *d* does not affect the chemical states significantly.



**Figure S5.** X-ray photoelectron (XP) Ti 2p, Zr 3d, N 1s and O 1s spectra of  $Ti_{0.8}Zr_{0.2}O_xN_y$  catalyst. The spectra (solid curves) are shown with deconvolutions into several peaks (dashed curves) after subtracting Shirley-type backgrounds (dash-dotted curves).



**Figure S6.** XP Ti 2p spectra of  $Ti_{0.8}Zr_{0.2}O_xN_y$  catalyst after five different total sputtering times,  $t_s$  for 1, 2, 3, 4 and 5 minutes. The spectra (solid curves) are shown with deconvolutions into six peaks (dashed curves) after subtracting Shirley-type backgrounds (dash-dotted curves).



**Figure S7.** X-ray photoelectron (XP) Ti 2p, Zr 3d, N 1s and O 1s spectra of  $Ti_{1-d}Zr_dO_xN_y$  catalysts for four different values of *d*: (i) 0.1, (ii) 0.2, (iii) 0.3 and (iv) 0.4 after N<sub>2</sub> pyrolysis at 1173 K for 2 h.

#### S5. Effect of pyrolysis temperature on ORR activity of Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalysts.

The RDE voltammograms of Ti<sub>1-d</sub>Zr<sub>d</sub>O<sub>x</sub>N<sub>y</sub> catalysts for three different N<sub>2</sub>-pyrolysis temperatures,  $T_1$  are shown in **Figure S8**. At  $T_1 = 1123$  K, the optimum temperature for the Zr-free TiO<sub>x</sub>N<sub>y</sub> catalyst,<sup>S11</sup> Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> exhibited higher ORR activity than TiO<sub>x</sub>N<sub>y</sub>. If the carbon residues from urea precursors formed active sites, TiO<sub>x</sub>N<sub>y</sub> and Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> should display identical activity as they were synthesized under identical conditions except for the addition of ZrCl<sub>4</sub> into the precursor dispersion. Therefore, the active sites are on the surface of Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub>, not carbon residues and Zr atoms increased the activity. The activity increases as  $T_1$  increases to 1173 K then decreases when  $T_1$  further increases to 1223 K. At the optimized  $T_1 = 1173$  K, Ti<sub>1-d</sub>Zr<sub>d</sub>O<sub>x</sub>N<sub>y</sub> catalysts were synthesized at four different d = 0.1, 0.2, 0.3 and 0.4. The activity was evaluated using a half-wave potential,  $E_{1/2}$ , the potential at which half of the limiting current density is obtained, whereas the selectivity was evaluated using a hydrogen peroxide yield,  $X_{H,O_1}$ . The results are summarized in **Table S1**. The optimum *d* both for activity and selectivity of the catalyst is 0.2; the highest  $E_{1/2}$  of 0.62 V and the lowest  $X_{H,O_1}$  of 0.9–1.5% are obtained.



**Figure S8.** RDE voltammograms for  $Ti_{0.8}Zr_{0.2}O_xN_y$  catalysts after three different N<sub>2</sub>-pyrolysis temperatures,  $T_1$ , at 1123 K, 1173 K and 1223 K. A RDE voltammogram of  $TiO_xN_y$  catalyst at  $T_1 = 1123 \text{ K}^{S12}$  is also shown as a reference. The scans are performed under N<sub>2</sub> and O<sub>2</sub> atmospheres using a rotation speed of 1500 rpm and a scan rate of  $-5 \text{ mV s}^{-1}$  (cathodic) in 0.1-mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. The catalyst loading for  $Ti_{0.8}Zr_{0.2}O_xN_y$  is set constant at 0.86 mg cm<sup>-2</sup> whereas that for  $TiO_xN_y$  is set at 1.00 mg cm<sup>-2</sup>.

**Table S1.** Half-wave potentials,  $E_{1/2}$  and hydrogen peroxide yields,  $X_{H_2O_2}$  of  $Ti_{1-d}Zr_dO_xN_y$  catalysts for four different d = 0.1, 0.2, 0.3 and 0.4 shown in **Figure 3**. The  $X_{H_2O_2}$  are shown at four different potentials E = 0.7, 0.6, 0.5 and 0.4 V.

Catalyst	$E_{1/2}$ vs. RHE	$X_{\rm H_2O_2}$   $E = 0.7 \rm V$	$X_{\rm H_2O_2}$   $E = 0.6 \rm V$	$X_{\rm H_2O_2}$   $E = 0.5 \rm V$	$X_{\rm H_2O_2}$   $E = 0.4 \rm V$
$Ti_{0.6}Zr_{0.4}O_xN_y$	0.38 V	11.8%	11.3%	11.2%	10.0%
$Ti_{0.7}Zr_{0.3}O_xN_y$	0.42 V	8.7%	8.9%	8.6%	7.0%
$Ti_{0.8}Zr_{0.2}O_xN_y$	0.62 V	1.4%	1.5%	1.2%	0.9%
$Ti_{0.9}Zr_{0.1}O_xN_y$	0.48 V	4.1%	4.8%	4.3%	3.2%

### S6. Effect of NH<sub>3</sub>-annealing temperature on the ORR activity of Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalysts.

A low temperature NH<sub>3</sub>-annealing maximizes the activity and nitrogen doping level of Zr-free TiO<sub>x</sub>N<sub>y</sub><sup>S11</sup> and TiO<sub>x</sub>N<sub>y</sub>P<sub>z</sub><sup>S13</sup> catalysts after optimizing the temperature. However, it does not increase the activity of Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalyst as shown in **Figure S9**. The atomic ratio of nitrogen to the sum of titanium and zirconium, i.e., *y* in Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> is determined by the XP spectra. The calculated *y* values are  $0.91 \pm 0.10$ ,  $0.90 \pm 0.03$ ,  $0.91 \pm 0.01$  and  $0.95 \pm 0.02$  for Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalyst before annealing, that after annealing at 873 K, 923 K and 973 K, respectively. The increase in *y* is limited and the resulting activity is not increased after the NH<sub>3</sub>-annealing. The ZrO<sub>2</sub> phase present in the Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalyst shown in **Figure 1(a)-ii** could consume reactive nitrogen from NH<sub>3</sub> gas<sup>S7</sup> and thus surface nitrogen content does not increase.



**Figure S9.** RDE voltammograms of  $Ti_{0.8}Zr_{0.2}O_xN_y$  catalyst before and after NH<sub>3</sub>-annealing at three different temperatures,  $T_2$ , at 873, 923 and 973 K. The scans are performed under N<sub>2</sub> and O<sub>2</sub> atmospheres using a rotation speed of 1500 rpm and a scan rate of  $-5 \text{ mV s}^{-1}$  (cathodic) in 0.1-mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. The catalyst loading is set constant at 0.86 mg cm<sup>-2</sup>.

#### S7. Optimization of synthesis conditions for the ORR activity of Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalysts.

Effects of NH<sub>3</sub>-annealing temperature and duration ( $T_2$  and t, respectively) on the ORR activity of Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalysts synthesized with phen are investigated. Their RDE voltammograms with various  $T_2$  and t are shown in **Figure S10**. The activity is successfully maximized at  $T_2 = 1073$  K and t = 3.0 h and the calculated y value is  $2.09 \pm 0.14$ , twice as large as that of phen-free Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalysts. The optimized Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalyst synthesized with phen exhibits an excellent durability against start-up/shut-down cycles as shown in **Figure 4** and the changes in  $E_{1/2}$  and kinetic current density,  $j_k$  are summarized in **Table S2**.



**Figure S10.** (left) RDE voltammograms of  $Ti_{0.8}Zr_{0.2}O_xN_y$  catalysts synthesized with phen after NH<sub>3</sub>annealing at three different  $T_2$ , 1023 K, 1073 K and 1123 K for a fixed t = 3 h and (right) those after NH<sub>3</sub>annealing at a fixed  $T_2 = 1073$  K for three different t, 2.0 h, 3.0 h and 4.5 h. The scans are performed under N<sub>2</sub> and O<sub>2</sub> atmospheres using a rotation speed of 1500 rpm and a scan rate of -5 mV s<sup>-1</sup> (cathodic) in 0.1mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. The catalyst loading is set constant at 0.86 mg cm<sup>-2</sup>.

**Table S2.** The ORR kinetic data of  $Ti_{0.8}Zr_{0.2}O_xN_y$  and  $TiO_xN_yP_z$  catalysts before and after 5,000 potential cycles between 1.0 V and 1.5 V shown in Figure 4.

	Before 5,000 cycles		After 5,000 cycles	
Catalyst	$E_{1/2}$ vs. RHE	$j_{\rm k} \mid E = 0.7  {\rm V}^*$	$E_{1/2}$ vs. RHE	$\dot{J}$ k $\mid E = 0.7 \text{ V}^*$
$Ti_{0.8}Zr_{0.2}O_xN_y$	0.66 V	$2.29 \text{ mA cm}^{-2}$	0.62 V	$0.90 \text{ mA cm}^{-2}$
$TiO_xN_yP_z$	0.63 V	$1.45 \text{ mA cm}^{-2}$	0.55 V	$0.37 \text{ mA cm}^{-2}$

\*Kinetic current density,  $j_k = |j| \cdot |j_l| \cdot (|j_l| - |j|)^{-1}$  at E = 0.7 V where  $j = j_O - j_N$  and  $j_l$  is the limiting current density.

### S8. Durability of Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>x</sub>N<sub>y</sub> catalysts against load cycles.

In fuel cell vehicles, the potential is in general controlled between 0.6 V and 1.0 V, corresponding to the highest load and idling mode, respectively.<sup>S14</sup> Durability of the best  $Ti_{0.8}Zr_{0.2}O_xN_y$  catalyst against the load 5,000 cycles is displayed in **Figure S11**. The activity remains almost the same after 5,000 cycles, which indicate that this catalyst is stable at  $E \le 1.0$  V.



**Figure S11.** RDE voltammograms of  $Ti_{0.8}Zr_{0.2}O_xN_y$  catalyst before (solid curve) and after (dash-dotted curve) 5,000 potential cycles between 0.6 and 1.0 V vs. RHE with symmetric rectangular waves shown in the inset: it was held at 0.6 V for 3 s then at 1.0 V for 3 s in 0.1-mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution. The catalyst was synthesized by two step heating process; it was first heated under N<sub>2</sub> at 1173 K for 2 h then heated under NH<sub>3</sub> at 1073 K for 3 h. Before and after the 5,000 cycles, scans were performed under N<sub>2</sub> and O<sub>2</sub> atmospheres using a rotation speed of 1500 rpm and a scan rate of  $-5 \text{ mV s}^{-1}$  (cathodic) to evaluate the activity.

Supporting references

- S1. Stamenković, V.; Schmidt, T. J.; Ross, P. N.; Marković, N. M. Surface Composition Effects in Electrocatalysis: Kinetics of Oxygen Reduction on Well-Defined Pt<sub>3</sub>Ni and Pt<sub>3</sub>Co Alloy Surfaces. *J. Phys. Chem. B* 2002, *106*, 11970–11979.
- S2 Robinson, K. S.; Sherwood, P. M. A. X-Ray Photoelectron Spectroscopic Studies of the Surface of Sputter Ion Plated Films. *Surf. Interface Anal.* 1984, 6, 261–266.
- S3 Saha, N. C.; Tompkins, H. G. Titanium Nitride Oxidation Chemistry: An X-ray Photoelectron Spectroscopy Study. J. Appl. Phys. 1992, 72, 3072–3079.
- Wang, J.; Yu, Y.; Li, S.; Guo, L.; Wang, E.; Cao, Y. Doping Behavior of Zr<sup>4+</sup> Ions in Zr<sup>4+</sup>-Doped TiO<sub>2</sub> Nanoparticles. J. Phys. Chem. C 2013, 117, 27120–27126.
- S5 Takano, I.; Isobe, S.; Sasaki, T. A.; Baba, Y. Nitrogenation of Various Transition Metals by N<sub>2</sub><sup>+</sup>-ion Implantation. *Appl. Sur. Sci.* 1989, *37*, 25–32.
- S6 Rizzo, A.; Signore, M. A.; Mirenghi, L.; Di Luccio, T. Synthesis and Characterization of Titanium and Zirconium Oxynitride Coatings. *Thin Solid Films* 2009, *517*, 5956–5964.
- S7 Chisaka, M.; Ishihara, A.; Morioka, H.; Nagai, T.; Yin, S.; Ohgi, Y.; Matsuzawa, K.; Mitsushima, S.; Ota, K. Zirconium Oxynitride-Catalyzed Oxygen Reduction Reaction at Polymer Electrolyte Fuel Cell Cathodes, *ACS Omega* 2017, *2*, 678–684.
- S8 Di Valentin, C.; Pacchioni, G.; Selloni, A.; Livraghi, S.; Giamello, E. Characterization of Paramagnetic Species in N-Doped TiO<sub>2</sub> Powders by EPR Spectroscopy and DFT Calculations. J. Phys. Chem. B 2005, 109, 11414–11419.
- Wang, J.; Zhu, W.; Zhang, Y.; Liu, S. An Efficient Two-Step Technique for Nitrogen-Doped Titanium Dioxide Synthesizing: Visible-Light-Induced Photodecomposition of Methylene Blue. J. Phys. Chem. C 2007, 111, 1010–1014.

- S10 Yang, G.; Jiang, Z.; Shi, H.; Xiao, T.; Yan, Z. Preparation of Highly Visible-Light Active N-Doped TiO<sub>2</sub> Photocatalyst. J. Mater. Chem. 2010, 20, 5301–5309.
- S11 Chisaka, M.; Yamamoto, Y.; Itagaki, N.; Hattori, Y. Active Site Formation for Oxygen Reduction Reaction on Carbon-Support-Free Titanium Oxynitride with Boosted Activity in Acidic Media, ACS Appl. Energy Mater. 2018, 1, 211–219.
- S12 Chisaka, M.; Morioka, H. Phosphor and Nitrogen Co-doped Rutile TiO<sub>2</sub> Covered on TiN for Oxygen Reduction Reaction in Acidic Media, *Catal. Sci. Technol.* **2019**, *9*, 611–619.
- S13 Chisaka, M.; Xiang, R.; Maruyama, S.; Daiguji, H. Efficient Phosphorus Doping into the Surface Oxide Layers on TiN to Enhance Oxygen Reduction Reaction Activity in Acidic Media, ACS Appl. Energy Mater. 2020, 3, 9866–9876.
- S14 Ohma, A.; Shinohara, K.; Iiyama, A.; Yoshida, T.; Daimaru, A. Membrane and Catalyst Performance Targets for Automotive Fuel Cells by FCCJ Membrane, Catalyst, MEA WG. *ECS Trans.* 2011, *41*, 775–784.