Supporting Information for

Active Pt nano-coated layer with Pt-O-Ce bond on CeOₓ nanowire cathode formed by electron beam irradiation

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Figure S1 shows morphology and element analysis data observed for as-prepared CeO$_x$ nanowire (NW).

**Figure S1** STEM-EDS analysis results of as-prepared CeO$_x$ NW using low magnification STEM images: (a), (b), dark field image: (c), Ce L mapping image: (d), and O K mapping image: (e).

Next, TEM and spectra acquisition parameters are shown below.
Camera and detector type: Gatan OneView (Bright field TEM images)

For bright field TEM image observation:
- Size in Pixels: 4096 x 4096, Pixel Size: 0.55 nm x 0.55 nm
- Beam current at 200 kV: approximately 113 µA
- Condenser lens (CL) apertures size for elemental mapping: 40 µm
- Convergence Semi-angle: 14 mrad
Figure S2 presents high resolution image observed for as prepared CeO\textsubscript{x} NW. This high-resolution image indicates that CeO\textsubscript{x} NW consists of nano-sized CeO\textsubscript{x} particles whose particle size is approximately 4 or 5 nm.

![Figure S2: High resolution TEM image observed for CeO\textsubscript{x} NW.](image)

**Figure S2**  High resolution TEM image observed for CeO\textsubscript{x} NW.
Figure S3 shows STEM image and EDS elemental mapping data observed for the sample which was prepared in the conditions of electron beam dose level = 100 kGy and C₂H₅OH/ K₂PtCl₄ molar ration = 5. Small amount of Pt particles was deposited on CeOₓ NW surface.

**Figure S3** STEM-EDS analysis data using dark field image: (a), and element analysis map: (b) including combination map of Pt M map, O K map and Ce L map observed for Pt nano-coated CeOₓ NW/ C (Pt/C=0.2).

Electron beam dose level: 100 kGy,  C₂H₅OH /K₂PtCl₄ molar ratio = 5
Figure S4 shows STEM image and EDS elemental mapping data observed for the sample which was prepared in the conditions of electron beam dose level $= 1$ MGy and $\text{C}_2\text{H}_5\text{OH}/\text{K}_2\text{PtCl}_4$ molar ratio $= 5$. Big grain growth of Pt particles was observed.

**Figure S4** STEM-EDS analysis data using dark field image: (a), and element analysis map: (b) including combination map of Pt M map, O K map and Ce L map observed for Pt nano-coated CeO$_x$ NW/ C (Pt/C=0.2).

Electron beam dose level: 1 MGy, $\text{C}_2\text{H}_5\text{OH}/\text{K}_2\text{PtCl}_4$ molar ratio $= 5$
Figure S5 shows TEM and STEM images observed for sample which was prepared in the condition of \( \text{C}_2\text{H}_5\text{OH}/\text{K}_2\text{PtCl}_4 \) molar ration = 0.5. The sub nano-sized Pt particles were homogeneously dissolved into CeO\(_x\) NW.

**Figure S5** TEM and STEM images observed for Pt-CeO\(_x\) NW (Pt content: 20 wt%), high resolution TEM image (a), high resolution TEM image (b), and dark field image (c). Electron beam dose level: 500 kGy, \( \text{C}_2\text{H}_5\text{OH}/\text{K}_2\text{PtCl}_4 \) molar ratio = 0.5
Figure S6 demonstrates line scan analysis data of Pt and Ce and dark field image observed for the thin area of sample which was prepared in the condition of C$_2$H$_5$OH/ K$_2$PtCl$_4$ molar ration = 0.5. We concluded that Pt particles were homogeneously dissolved into CeO$_x$ NW together with the results of Figure 3.

**Figure S6** Line scan charts for element analysis using EDS analysis method and its analysis area of the sample in the dark field image.
Figure S7 shows Pt 4f and Ce 3d spectra taken from the sample which was prepared using sodium tetrahydroborate (NaBH₄) as reducing agent of K₂PtCl₄. Pt-O-X (X: Ce or oxygen vacancy) was observed in Pt 4f spectrum as well as sample with nano-coated layer on CeOₓ NW.

**Figure S7** XPS Pt 4f and Ce 3d spectra recorded from nanosized Pt-CeOₓ NW/ C which was prepared using conventional chemical reduction method. Pt-O-X (X: Ce cation or oxygen vacancy).
Figure S8 presents XPS Ce 3d spectrum taken from CeO$_x$ NW/C. As shown in this figure, the small amount of Ce$^{3+}$ species was observed on the surface of CeO$_x$ NW without Pt.

Figure S8 XPS Ce 3d spectrum taken from CeO$_x$ NW/ C.
Figure S9 presents TEM-EDS analysis data observed for nano-sized Pt loaded CeO$_x$ NW/C sample. Some small Pt parties were dispersed on CeO$_x$ NW surface without nano-coated layer.

**Figure S9** Dark field image and EDS analysis data (i.e., O K mapping image, Ce L mapping image, and Pt L mapping image) observed for nano-sized Pt-CeO$_x$ NW/C (Pt/C=0.2) which was prepared using conventional chemical reduction method.
Figure S10 presents polarization curve and Tafel plot derived from the polarization curve which was obtained from MEA using conventional nano-sized Pt/C. This data was obtained at 140 h after start of fuel cell operation. The activation overpotential at 100 mAcm$^{-2}$ (after 140h operation) estimated from the linear regression equation (refer to Figure S10(b)) in the Tafel region obtained from the MEA using conventional nano-sized Pt/C was 0.17 V.

**Figure S10** Polarization curve at 140 h operation (a) recorded from conventional nano-sized Pt /C (a) and Tafel plot derived from polarization curve (b).
Figure S11 presents polarization curve and Tafel plot derived from the polarization curve which was obtained from MEA using nano-sized Pt loaded CeO\(_x\) NW/C. This data was obtained at 80 h after start of fuel cell operation. The activation overpotential at 100 mA\(\text{cm}^{-2}\) (after 80 h operation) estimated from the linear regression equation (refer to Figure S11(b)) in the Tafel region obtained from the MEA using nano-sized Pt loaded CeO\(_x\) NW/C cathode was 0.18 V.

**Figure S11** Polarization curve at 80 h operation (a) recorded from nano-sized Pt loaded CeO\(_x\) NW/C and Tafel plot derived from polarization curve (b). (electron beam dose amounts: 500 kGy, C\(_2\)H\(_5\)OH /K\(_2\)PtCl\(_4\) molar ratio = 0.1
Figure S12 demonstrates the operation time dependence of MEA performances observed for Pt-CeO$_x$ NW/ C samples which were fabricated under less electron dose amount (i.e., 100 kGy) and excess dose amount (i.e., 1 MGy). The observed cell potential at 100 mA cm$^{-2}$ were in low level as compared with Pt nano-coated CeO$_x$ NW/ C which was fabricated based on the optimal electron beam irradiation condition.

![Graph showing cell potential dependence on operation time](image)

**Figure S12** Cell potential (IR-free) dependence of operation time of MEA observed for Pt-CeO$_x$ NW/ C fabricated by electron beam irradiation method. (electron beam dose amounts: 100 kGy (▼) and 1 MGy (▲)). C$_2$H$_5$OH /K$_2$PtCl$_4$ molar ratio = 5
Figure S13 shows the super cell of model surface of CeO$_2$ (111) for (1x1) surface, (1x2) surface and (1x3) surface which is used in the present surface first-principles calculation.

**Figure S13** Model surface of CeO$_2$ (111) for (1x1), (1x2) and (1x3) super cells.
Figure S14 shows the stable water adsorption model on CeO$_2$ (111) surface which is calculated using (1x1), (1x2) and (1x3) super cell in the present first-principles calculation.

**Figure S14** Adsorption model of water on CeO$_2$ (111) surface for or (1x1), (1x2) and (1x3) super cells.
Figure S15 presents surface lattice defect models in (1 x 1), (1 x 2), and (1x3) super cells.

**Figure S15** Surface models of lattice defect of Pt cation (Pt$^{''}_{\text{Ce}}$ - V$_{\text{o}}^{-}$) in (1 x 1) super cell, lattice defect of Ce cation (2Ce$^{'}_{\text{Ce}}$ - V$_{\text{o}}^{-}$) in (1 x 2) super cell, and Pt$^{2+}$ cluster (2Ce$^{'}_{\text{Ce}}$ - Pt$^{''}_{\text{Ce}}$ - 2V$_{\text{o}}^{-}$) in (1 x 3) super cell.
Figure S16 presents surface water adsorption models on lattice defect in (1 x 1), (1 x 2), and (1 x 3) super cells.

![Diagram showing surface water adsorption models](image)

**Top view** | **Front view**
---|---
(a) (1x1) surface | Hydrogen bond 1.97 Å 0.98 Å
(b) (1x2) surface | Hydrogen bond 1.00 Å 2.00 Å
(c) (1x3) surface | Hydrogen bond 0.97 Å 1.01 Å

**Figure S16** Surface water adsorption models on lattice defect of Pt cation (Pt\textsuperscript{′′}\textsubscript{Ce} - V\textsubscript{O}\textsuperscript−) in (1 x 1) super cell: (a), lattice defect of Ce cation (2Ce\textsuperscript{′}\textsubscript{Ce} - V\textsubscript{O}\textsuperscript−) in (1 x 2) super cell: (b), and Pt\textsuperscript{2+} cluster (2Ce\textsuperscript{′}\textsubscript{Ce} - Pt\textsuperscript{′′}\textsubscript{Ce} - 2V\textsubscript{O}\textsuperscript−) in (1 x 3) super cell: (c).