Design of Pt-CeO$_x$ hetero-interface on electrodes in polymer electrolyte membrane fuel cells

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Abstract. Pt-CeO$_x$ interface on Pt electrodes was prepared for improvement of both oxygen reduction reaction (ORR) activity of Pt cathode and CO tolerance of Pt anode. The surface of Pt-CeO$_x$ nano-particle/C electrode mainly consists of metallic Pt, ionized Pt (i.e. Pt$^{2+}$) and Ce$^{3+}$ species. The ORR activity on Pt was improved by the formation of Pt-CeO$_x$ interface. In-situ XAFS analysis suggests that cerium oxide surface in the Pt-CeO$_x$/C was oxidized instead of Pt surface by electrochemical redox reaction of CeO$_x$ at room temperature. This suggests that the Pt-CeO$_x$ interface plays key role for improvement of cathode performance. Also, CO tolerance of Pt was improved by the formation of aforementioned interface. The improvement of CO tolerance of Pt was also observed by using in-situ IR analysis. Based on all experimental data, it is concluded that the design of defect structure in Pt-CeO$_x$ provides us opportunity to make the breakthrough electrodes for fuel cell application.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been developed as clean and efficient power sources for generating electricity by using hydrogen and oxygen. In the case of PEMFCs using Nafion$^\text{®}$ membrane, the IR loss of electrolyte membrane and anodic over-potential loss are in small level when operation temperature of PEMFCs are under 90ºC. In contrast, the over-potential loss at cathode is large because of slow kinetics of oxygen reduction reaction (ORR) on Pt electrode as shown in figure 1(a). If small amount of carbon monoxide (CO) existed in the hydrogen, the over-potential loss on the anode becomes large (figure 1(b)). It is CO poisoning on Pt anode. For development of...
high quality PEMFC devices, aforementioned both slow kinetics of ORR and CO tolerance of Pt have to be improved.

\[ \text{Figure 1. Relationship between cell potential and current density at } 80^\circ\text{C; (a): fuel does not include carbon monoxide, (b): fuel includes carbon monoxide more than 3ppm.} \]

For this challenge, the authors focused on the role of heterogeneous interface of Pt and ceria (CeO\(_x\)) on Pt electrodes in PEMFCs. The ORR activity on Pt in Pt-CeO\(_x\)/conductive carbon (C) was firstly examined by Yu et al. [1] for development of direct methanol fuel cells (DMFCs). 10wt% CeO\(_x\) doped Pt/C exhibited the good performance by using single cell of DMFCs. Takahashi et al. [2] reported that the ORR activity on the Pt-CeO\(_x\)/C was higher than commercially available Pt/C cathode in the operation condition of PEMFCs. Lim et al. [3] suggested that the active oxygen supplied from CeO\(_x\) on Pt surface contributed to the improvement of the ORR activity of the Pt-CeO\(_x\)/C cathode.

On the other hand, CO tolerance effect of Pt promoted by CeO\(_x\) has been actively investigated because of unique properties of CeO\(_x\) such as oxygen storage property, surface basicity, and electrochemical redox reaction between Ce\(^{4+}\) and Ce\(^{3+}\) in CeO\(_x\) at elevated temperature. The overview of proposed mechanism in previously reported papers was given by our short review paper. [4] But the roles of CeO\(_x\) in the Pt-CeO\(_x\) interface on the cathodes and anodes are still unclear.

In the present work, we try to improve the ORR activity on Pt-CeO\(_x\)/C cathode and CO tolerance of Pt in Pt-CeO\(_x\)/C anode, also the detail defect structure of Pt-CeO\(_x\) interface was characterized by using TEM and XPS. To conclude the defect structural feature well, atomistic simulation was performed by using GULP code, interatomic potential and shell model. Based on those results, we made Pt-CeO\(_x\) nanowire/C electrodes and examined the electrochemistry on the electrodes for development of high quality cathode and anode materials.

2. Experimental

Pt-CeO\(_x\) nano-sized particle/C electrodes were prepared in a stepwise process. The pure CeO\(_2\) powder was synthesized by a hot ammonium carbonate precipitation method. The starting materials
used were commercially available cerium nitrate (Ce(NO$_3$)$_3$•6H$_2$O, Kanto Chemical Company, Japan) and ammonium bicarbonate ((NH$_4$)$_2$CO$_3$, Wako Pure Chemical Industries, Japan) powders. The Ce(NO$_3$)$_3$•6H$_2$O powder was dissolved into distilled water. To prepare the fine precipitation, a (NH$_4$)$_2$CO$_3$ aqueous solution was heated at 58.0$^\circ$C in a thermostatic chamber. The Ce(NO$_3$)$_3$ aqueous solution was dropped into the (NH$_4$)$_2$CO$_3$ aqueous solution for 1h period. And the mixture was continuously stirred using magnetic stirrer at 58$^\circ$C for 24h. After filtration and rinsing, the precipitate was dried at room temperature in a N$_2$ gas flow. The dried powders were calcined at 400 $^\circ$C for 2h in an O$_2$ gas flow. The CeO$_x$ nanowire was synthesized by using an alcohol thermal method. The starting materials used were commercially available cerium chloride (CeCl$_3$•H$_2$O, Nacalai Tesque Company, Japan), cetyltrimethylammonium bromide (C$_{16}$H$_{33}$BrN, Wako Pure Chemical Industries, Ltd., Japan) and urea ((H$_2$N)$_2$CO, Nacalai Tesque Company, Japan) powders. Powders were dissolved in dehydrated ethanol and mixed using a magnetic stirrer at room temperature for one hour under a dry nitrogen atmosphere. C$_{16}$H$_{33}$BrN and (H$_2$N)$_2$CO were respectively used as surfactant for micelle formation and as base for control of pH during the reaction. The reaction mixture was filtered by ultrafiltration and half the filtrate was transferred to a 25ml Teflon autoclave. CeO$_x$ nanowire synthesis was performed by heating the 25ml Teflon autoclave at 80$^\circ$C for 4 days in a heating oven. After filtration and rinsing, the mixture was dried at room temperature in a N$_2$ gas flow. To impregnate fine Pt particles on pure CeO$_2$ particles, hexachloroplatinic(IV) acid (H$_2$PtCl$_6$•6H$_2$O) powder was dissolved in ethanol at the glove box where the moisture level was kept below 10ppm. The previously prepared pure CeO$_2$ powders were dispersed in the H$_2$PtCl$_6$ ethanol solution and dried in the glove box. The dried mixture was calcined at 400 $^\circ$C for 1h in a 10% H$_2$/He gas flow. For preparation of Pt-CeO$_x$ nanowire/C electrodes, potassium hexachloroplatinate (IV) (K$_2$PtCl$_6$•H$_2$O, Sigma-aldrich Ltd., Japan) powder was dissolved in distilled water and stirred for one hour. The aqueous K$_2$PtCl$_6$ solution was added to a suspension of the previously prepared CeO$_x$ nanowires dispersed in distilled water. The resulting mixture was left standing at room temperature for 12h. The platinum complex in the mixture was reduced at room temperature for 1h in aqueous sodium borohydride (NaBH$_4$, Sigma-aldrich Ltd., Japan) solution. The mixture was rinsed with water and ethanol, and then it was dried at room temperature in nitrogen atmosphere. In the final stage, the prepared Pt-CeO$_x$ and C were dispersed in ethanol and dried in a N$_2$ gas flow.

The crystal phases of Pt-CeO$_x$/C were identified by selected area electron diffraction analysis and X-ray diffraction analysis. The particle size and particle morphology were measured by TEM. The TEM observation was performed by using JEM-2000EX/T (JEOL, Co. Ltd, Japan) electron microscope operated at 200 kV. The surface chemical states of Pt-CeO$_x$/C were examined by using hard X-ray photoelectron spectroscopy (HXPS) for average chemical states analysis of the interface and soft X-ray photoelectron spectroscopy (SXPS) for chemical states analysis of the top surface.

To characterize the CO poisoning phenomena on Pt anode, in-situ FT-IR analysis was performed. The electrolyte solution used was the 0.5M H$_2$SO$_4$ solution saturated with Ar for 10min. Pure CO gas
was purged into the electrolyte solution at 0.07V for 30min to obtain an equilibrium adsorption of CO. CO in the bulk solution was then removed by purging with Ar while keeping 0.07V for 5min. IR measurement was carried out from 0.07 to 1.07V. The potential shifts were every 50mV interval. And the spectral resolution used was 2cm⁻¹.

The cathode property of Pt-CeOₓ/C was examined by linear voltammetry in 0.5M H₂SO₄ aqueous solution in the potential ranging from 0.95 to 0 V (V vs. Ag/AgCl). Anode properties of Pt-loaded CeOₓ nanowire mixed with C were examined by cyclic voltammetry (CV) in mixed aqueous solution of 0.5M CH₃OH and 0.5M H₂SO₄ in the potential ranging from 0 to 1.5V (vs. Ag/AgCl). The electrochemical measurements were carried out using a standard three-electrode glass cell with a rotating disk electrode after that had a pre-treatment by heating at a 28 °C. A Pt foil and Ag/AgCl were used as a counter and reference electrodes, respectively. The measured potentials were converted to the reversible hydrogen electrode (RHE) scale. Prior to the electrochemical measurements, the electrochemical pre-treatment for conditioning of the anode surface was carried out by means of 30 cycle sweeps in the potential range from 0 to 1.5V (vs. Ag/AgCl).

3. Results and discussion

The TEM photograph of as prepared Pt-CeOₓ/C is presented in figure 2. On the selected area electron diffraction pattern (SAEDP) taken from as prepared samples, the diffraction rings belong to metallic platinum and fluorite structured ceria. The Pt particles were mainly situated on well crystalline ceria particles and Pt particles partially embedded into ceria particle. [5]

![Figure 2. TEM photograph and selected area electron diffraction pattern (SAEDP) taken from as prepared sample. (a): general image and SAEDP. (b) Magnified image and FFT patterns.](image)

However, the chemical composition and general view of Pt-CeOₓ/C electrode were conspicuously changed after the electrochemical pre-treatment for conditioning of the electrode surface. As shown in figure 3, small amount low CeOₓ partially covered the Pt surface. On SAEDP taken from this sample, the careful analysis of SAED patterns revealed that the short-range ordered materials and nano-crystallites in the residual oxides could include fluorite-structured ceria (CeO₂, d(111) ≈ 3.1 Å),
Figure 3. TEM photograph (a), selected area electron diffraction pattern (b) and Ce3d spectra taken from electrochemically pre-treated Pt-CeO$_2$/C electrode.

Reduced ceria (Ce$_2$O$_3$, d$(111)$ ≈ 3.2-3.4 Å), PtO, and other compounds that were difficult to identify at this stage. Those microanalysis results suggest that free CeO$_2$ without Pt-CeO$_x$ interaction is resolved into H$_2$SO$_4$ aqueous solution after 30 cycle sweeps in the potential range from 0 to 1.5V (vs. Ag/AgCl). It is concluded that Schottky type Pt$_{Ce}\cdot$ 2Vo$^{--}$-Ce$_{Ce}^+$ defect clusters were formed in the Pt-CeO$_2$ interface in our preparation process. [6] We expect that the electrode performance of Pt-CeO$_2$/C will be enhanced by the formation of aforementioned heterogeneous Pt-CeO$_2$ interface on Pt.

The ORR activity observed for conventional Pt/C and Pt-CeO$_2$/C were examined by using Tafel plots. The intersect point of Tafel line and potential axis in the Tafel plots reflects the level of exchange current density of ORR on the electrodes. If aforementioned intersect point shifted in the high potential region, the ORR activity is in high level. After the electrochemical pre-treatment, the ORR activity observed for Pt/C was slightly improved by enhancement of surface area of Pt.

Figure 4. Tafel plots obtained from conventional Pt/C (a) and Pt-CeO$_2$/C (b) electrodes.

In contrast, the ORR activity on Pt-CeO$_2$/C was conspicuously improved after the electrochemical pre-treatment. [7,8] Also, aforementioned intersect point observed for electrochemically pre-treated Pt-CeO$_2$/C was much higher than that of conventional Pt/C. This clearly indicates that the ORR activity on Pt in Pt-CeO$_2$/C was improved by the formation of Pt-CeO$_2$ hetero-interface.
To conclude why the surface of Pt in Pt-CeO\textsubscript{x}/C is active in cathode reaction, in-situ electrochemical X-ray absorption fine structure (XAFS) analysis was performed by using home-made electrochemical cell in synchrotron beam line (BL14B1 of SPring-8). In-situ XAFS measurements at the Pt L\textsubscript{3} and Ce L\textsubscript{3} absorption edges of the Pt–CeO\textsubscript{x}/C catalyst suggested that oxide formation on Pt was suppressed by the presence of CeO\textsubscript{x} as Ce\textsuperscript{3+} was oxidized to Ce\textsuperscript{4+} instead of Pt surface in cathodic condition. The electrochemistry observed for Pt-CeO\textsubscript{x}/C agreed with this result well. Based on those results, we conclude that the inhibition of Pt oxide formation is considered to be the primary factor for enhancement of the ORR activity on Pt in Pt-CeO\textsubscript{x}/C because ORR activity of the Pt oxide surface is much lower than that at the bare Pt surface. [9]

Since the formation of defect structure in Pt-CeO\textsubscript{x} interface is key for design of high quality cathode, the CeO\textsubscript{x} nanowires instead of CeO\textsubscript{x} nanoparticles were prepared by using alcohol thermal method. [10] SEM micrographs shown in figure 5 indicate that the product was composed of only nanowires. Also the average diameter of CeO\textsubscript{x} nanowires was approximately 35 nm. The aspect ratio of the fabricated CeO\textsubscript{x} nanowires was greater than 100. Electron diffraction rings can be assigned to CeO\textsubscript{2} (i.e. CeO\textsubscript{2} \((d(111) \approx 3.1 \ \text{Å}, \ d(200) \approx 2.7 \ \text{Å}, \ d(220) \approx 1.9 \ \text{Å})\) ) in the SAEDP on SEM image of figure 5. We concluded that the nano-scale surface roughness of CeO\textsubscript{x} nanowires makes them suitable for preparation of functional interfaces between nanosized Pt and CeO\textsubscript{x} nanowire surfaces. After the preparation of CeO\textsubscript{x} nanowires, Pt-CeO\textsubscript{x} nanowire/C electrode was prepared. The surface analysis of electrochemically pre-treated Pt-CeO\textsubscript{x} nanowire/C suggests that the electrode surface mainly consists of Pt (i.e. metallic Pt), ionized Pt (i.e. Pt\textsuperscript{2+}) and Ce\textsuperscript{4+} species. This suggests that the Pt-CeO\textsubscript{x} interface observed for Pt-CeO\textsubscript{x} nanowire/C is different from the case of Pt-CeO\textsubscript{x} nanoparticle/C. The Frenkel type defect structure would be formed in the Pt-CeO\textsubscript{x} interface on Pt-CeO\textsubscript{x} nanowire/C electrode. After 300 cycle sweeps in electrochemical pre-treatment process, the stationary state condition was observed in the case of Pt-CeO\textsubscript{x} nanowire/C. The ORR activity was observed by using 5wt% Pt-CeO\textsubscript{x}
The intersect point of Tafel slop and potential axis at 0.3 mA cm\(^{-2}\) in Tafel plot observed for 5wt\% Pt-CeO\(_x\) nanowire/C was almost same to aforementioned intersect point observed for 20wt\% Pt-CeO\(_x\) nanoparticle/C cathode. This suggests that we can reduce the Pt content from 20wt\% to 5wt\% in our Pt-CeO\(_x\) cathode by enhancement of ORR activity on our electrode.

For development of our design concept regarding metal–oxide hetero-interface on electrodes in fuel cell reaction, we examined the electro-oxidation reaction of methanol on conventional Pt/C and Pt-CeO\(_x\) nanowire/C anodes as well as ORR activity on cathodes. [10] The estimated onset potential of the commercially available 20wt\% Pt/C anode was approximately 0.5 V (vs. RHE). This is similar to the previously reported value observed for Pt/C (i.e. 0.5 V vs. RHE). [11] In contrast, the methanol electro-oxidation on 5wt\% Pt-loaded CeO\(_x\) nanowire/C commenced from approximately 0.19 V (vs. RHE), which is much lower than that of the aforementioned commercially available Pt/C. Also, this onset potential observed for Pt–CeO\(_x\) nanowire/C was conspicuously lower than previously reported PtRu–CeO\(_x\) nano-particle/C (0.30 V vs. RHE) [12] under similar experimental condition. Those data clearly indicates that CO tolerance of Pt in Pt–CeO\(_x\) can be improved by the formation of Pt-CeO\(_x\) interface on Pt anode.

To examine the influence of the CO poisoning phenomenon on the formation of Pt–CeO\(_x\) interface, CO desorption behaviour from Pt surface under applied potential was observed by using in-situ IR analysis method (figure 6). The absorption band at 2106 cm\(^{-1}\) corresponds to the adsorbed CO on Au electrode. Alternatively, the strong absorption bands at 2030 cm\(^{-1}\) and 2012 cm\(^{-1}\) in figure 6(a) and 2046 cm\(^{-1}\) and 2017 cm\(^{-1}\) in figure 6(b) were assigned to the linear bonded CO on Pt. The bridged (doubly coordinated) CO on Pt was observed at 1842 cm\(^{-1}\) in 1856 cm\(^{-1}\) in this figure. In the present analysis, at 70 mV (vs. RHE), the center of band spectra for adsorbed CO on Pt in Pt-CeO\(_x\)/C conspicuously shifted in higher wavenumber region as compared with those for adsorbed CO on Pt in the Pt/C. It suggests that the adsorbed strength of CO molecule on Pt surface becomes weak by formation of Pt-CeO\(_x\) interface on Pt. This supported the results of observation of onset potential of methanol oxidation. In addition, our atomistic simulation suggests that the defect structures in the interfaces on Pt-CeO\(_x\) nano-particles/C and Pt-CeO\(_x\) nanowire/C mainly consists of Schottky type defect (i.e. Pt\(_{Ce}^{"-}\). 2Vo\(^-\). Ce\(_{Ce}\)^\(^+\)) and Frenkel type defect (i.e. 2Pt\(^1\). 4O\(^-\). 4V\(_o\)^\(^-\). V\(_{ce}\)^\(^+\)), respectively. In the present manuscript, Kröger–Vink notation is used for simple

![Figure 6. In-situ FT-IR spectra taken from conventional Pt/C (a) and Pt-CeO\(_x\)/C (b).](image-url)
explanation of defect formation. Moreover, our atomistic simulation suggests that aforementioned clusters were just building unit for development of large defect clusters in the Pt-CeO$_x$ interface on Pt electrode. Also, our TEM analysis supported the results of atomistic simulation in the present work.

Based on all experimental results, we concluded that defect interface structure design in the interface is quite important for development of anode and cathode for fuel cell application.

4. Conclusion

For improvement of ORR activity on Pt and CO tolerance of Pt, Pt-CeO$_x$/C cathodes and anodes were prepared by a combined process of precipitation and impregnation method. Also, the Pt-CeO$_x$ interface was characterized by using TEM, XPS, in-situ XAFS and in-situ IR. To conclude the detail defect structure of interface, atomistic simulation was performed. Based on all experimental results, it is concluded that the present work is promising to provide both a rational strategy for design of metal-oxide interface which promotes electrode performance and high quality cathode and anode for fuel cells.

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