Room temperature redox reaction by oxide ion migration at carbon/Gd-doped CeO$_2$ heterointerface probed by an in situ hard x-ray photoemission and soft x-ray absorption spectroscopies

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Abstract

In situ hard x-ray photoemission spectroscopy (HX-PES) and soft x-ray absorption spectroscopy (SX-XAS) have been employed to investigate a local redox reaction at the carbon/Gd-doped CeO$_2$ (GDC) thin film heterointerface under applied dc bias. In HX-PES, Ce3d and O1s core levels show a parallel chemical shift as large as 3.2 eV, corresponding to the redox window where ionic conductivity is predominant. The window width is equal to the energy gap between donor and acceptor levels of the GDC electrolyte. The Ce M-edge SX-XAS spectra also show a considerable increase of Ce$^{3+}$ satellite peak intensity, corresponding to electrochemical reduction by oxide ion migration. In addition to the reversible redox reaction, two distinct phenomena by the electrochemical transport of oxide ions are observed as an irreversible reduction of the entire oxide film by O$_2$ evolution from the GDC film to the gas phase, as well as a vigorous precipitation of oxygen gas at the bottom electrode to lift off the GDC film. These in situ spectroscopic observations describe well the electrochemical polarization behavior of a metal/GDC/metal capacitor-like two-electrode cell at room temperature.

Keywords: hard x-ray photoemission spectroscopy, ionics, redox reaction, atomic switch, atom transistor, ReRAM
transmission electron microscopy [1]. Let us consider the case where an electrical potential is applied to a capacitor-like metal/insulator/metal (MIM)-type cell with an oxide ion (O\textsuperscript{2–}) applied to a semiconductor (electronic/hole conductor) and (b) ionic conductor. Assumed is d\(\mu_e\) = 0 in the extrinsic region, and d\(\mu_e\) ≠ 0 for the intrinsic region in the equation d\(E = \frac{\Delta\mu_e}{F}\). For simplicity, any kinetic feature at the electrode/GDC electrolyte interface is ignored.

1. Introduction

Ion migration in a strong applied electric field is a key phenomenon in the emerging new classes of nanoelectronic devices, especially in resistance random access memory (ReRAM) [1–4], atomic switch [5–7], atom transistor [8] and related memory devices, where electrochemical redox reactions play a crucial role in the generation and annihilation of highly electrically conductive filaments [2, 9, 10], metal nanobridges [5–8] or conductive suboxide at the interface [3]. Various attempts have been carried out using transmission electron microscopy [9, 10], atomic force microscopy [11] and other microscopy techniques to find experimental evidence that such switching behavior is caused by ion migration even at room temperature, through this ion transport is extremely slow at ambient temperatures. Now, atomistic pictures of the conducting path formation are becoming evident, supported by indirect observations for some devices to date, while most of the proposed models still include a certain amount of speculation. Few works have been done from the viewpoint of solid-state electrochemistry [11, 12], but ambiguities still remain to a considerable extent for the complete description of redox reaction and the resultant modulation of the electronic structure in nanospace, despite its crucial importance in the quest for an origin of the switching phenomena.

1.1. Theoretical background

Let us consider the case where an electrical potential is applied to a capacitor-like metal/insulator/metal (MIM)-type cell with an oxide ion (O\textsuperscript{2–})-electron/hole mixed conducting oxide of Gd-doped CeO\textsubscript{2} (GDC) as follows:

\[
\text{metal}(P_{\text{O}_2}^{\text{L}})(\text{Gd-doped CeO}_2 (O^{2–}+e^–))|C(P_{\text{O}_2}^{\text{R}})).
\]

The electrochemical potential of electrons (\(\mu_e\)) in the electrolyte, which is identical to the Fermi level, can be expressed as follows, if we assume that electrons in GDC are localized in a framework of an ideal dilute solution model of the electron, where activity coefficient of the electron is unity:

\[
\begin{align*}
\tilde{\mu}_e & = \mu_e - F\phi = (\mu_e^0 + RT \ln n) - F\phi. \\
\mu_e & = \mu_e^0 \quad \text{and} \quad F & = \text{the chemical potentials of the electron and Faraday constant, respectively,} \\
\phi & = \phi_{\text{sur}} + \phi_{\text{ext}}, \quad \text{in which} \phi_{\text{sur}} \text{ and} \phi_{\text{ext}} \text{ are the surface potential with reference to the surface and the electrical potential of the surface with reference to infinity induced by an external applied voltage (the Volta potential).}
\end{align*}
\]

If GDC is replaced by a doped semiconductor without any ionic conductivity, both linear \(\mu_e\) and \(\phi\) profiles would be anticipated as shown in figure 1(a), because of d\(\mu_e\) = 0 across the entire oxide film, resulting in d\(\tilde{\mu}_e\) = F d\(\phi\). Then, the system is regarded as a simple electrical conductor system in which the total electric current is expressed by Ohm’s law under a steady-state condition driven by the motive

\[P_{\text{O}_2} = P_0 / P^o, \quad \text{where} \quad P_0 \text{ and} P^o \text{ are the partial pressure of oxygen gas in Pa and the standard pressure of} \ 1.013 \times 10^5 \text{ Pa, respectively.}
\]
force of \(d\mu_{\text{e}}/dx\), assuming no electronic overvoltage at the interface, e.g. a Schottky barrier. On the other hand, if the ionic conductivity is present, the situation is completely changed and turns into an electrochemical polarization system comprised of an ion-electron/hole mixed conductor and ion-blocking/reversible electrodes.

GDC is well known as a good oxide-ion conductor under high oxygen activity conditions close to ambient pressures, due to the formation of \(V_{\text{O}}^{\bullet\bullet}\) to maintain the electroneutrality to compensate the acceptor dopant, which suggests that GDC is in an extrinsic region in the defect chemical viewpoint. The migration of the \(O^{2-}\) ion can be well described by that of oxygen vacancy (\(V_{\text{O}}^{\bullet}\)) as a quasi-particle. Its transport number of the oxide ion \(i_{\text{O}}\), defined as the fraction of the partial oxide ion current to the total current, is expected to be almost unity even around room temperature [13–16]. It is also well known that the partial ionic conductivity prevails under extremely reducing conditions or cathodically (negatively) polarized conditions. In contrast, the hole conductivity is expected to become predominant under extremely oxidizing or anodically (positively) polarized conditions, which is estimated to appear at \(P_{\text{O}_2} \gg 1\), due to increased hole concentration for the charge compensation to reduced oxygen vacancy [14].

If one side of the electrodes is the blocking electrode (BKE), the electrochemical polarization of the electrolyte occurs by \(O^{2-}\) ion migration in the vicinity of BKE under bias voltage application. Based on the classical viewpoint of electrochemical polarization under the condition where a steady state is attained, the electrochemical potential of \(V_{\text{O}}^{\bullet\bullet}\); \(\mu_{\text{vO}}\), satisfies \(d\mu_{\text{vO}} = 0\), resulting in the suppression of \(V_{\text{O}}^{\bullet\bullet}\) migration. If the defect chemical condition is in the extrinsic region, the \(V_{\text{O}}^{\bullet\bullet}\) concentration expressed as the site fraction of the GDC oxygen sublattice, \([V_{\text{O}}^{\bullet\bullet}]\), and the chemical potential of \(V_{\text{O}}^{\bullet\bullet}\) defined as \(\mu_{\text{vO}} = \mu_{\text{O}_2}^0 + RT \ln [V_{\text{O}}^{\bullet\bullet}]\) are both maintained at a constant value (\(d\mu_{\text{vO}} = 0\)). From the following reaction,

\[
2e^- + \frac{1}{2}O_2(g) + V_{\text{O}}^{\bullet\bullet} \rightarrow O_2^0,
\]

one can derive the equation for the local equilibrium condition below:

\[
2\mu_{\text{e}} + \frac{1}{2}\mu_{O_2(g)} + \mu_{\text{vO}} = \mu_{O_2^0}.
\]

Consequently, we end up with the relation

\[
d\mu_{\text{e}} = -\frac{i}{2}d\mu_{O_2(g)}, \quad \mu_{\text{O}_2} = 0,
\]

which suggests that the chemical potential of neutral oxygen gas, \(\mu_{\text{O}_2}\), in GDC is modulated by the applied external bias voltage. Finally, we find that \(d\phi = 0\), which corresponds to the strict Hebb–Wagner polarization condition because of \(d\mu_{\text{vO}} = d\mu_{\text{vO}} = 2F\phi = 0\) with \(d\mu_{\text{vO}} = 0\); as a conclusion, the applied voltage, \(E_{\text{app}}\), is solely related to \(\mu_{\text{e}}\) through \(dE_{\text{app}} = -d\mu_{\text{e}}/F = -d\mu_{\text{e}}/F\) as \(d\phi = 0\). The modulation of \(\mu_{\text{e}}\) at the BKE side is schematically shown in figure 1(b).

From equation (2), one can deduce the relation between \(E_{\text{app}}\) and the oxygen activity at the right-hand side (R) and the left-hand side (L) electrodes, \(P_{\text{O}_2}^{(R)}\) and \(P_{\text{O}_2}^{(L)}\), respectively, defined as the oxygen activity as follows:

\[
E_{\text{app}} = \frac{RT}{4F} \ln \frac{P_{\text{O}_2}^{(R)}}{P_{\text{O}_2}^{(L)}}. \quad (3)
\]

Both equation (3) and \(d\mu_{\text{vO}} = 0\) hold exactly, too, in the intrinsic region where \(n = 2 [V_{\text{O}}^{\bullet\bullet}] \propto P_{\text{O}_2}^{(O)}\), because of the attainment of the local equilibrium expressed by reaction (A), which results in variable \(\mu_{\text{vO}}\) and \(\mu_{\text{e}}\) against \(P_{\text{O}_2}\). However, a part of the bias voltage is compensated by the \(\mu_{\text{vO}}\) variation. Finally, we end up with \(E_{\text{app}}\) expressed as follows for the intrinsic region, since \(-d\phi = \frac{RT}{2F} \ln n\) deduced from \(d\mu_{\text{vO}} = 0\) and the electroneutrality condition of \(n = 2 \times (2[V_{\text{O}}^{\bullet\bullet}])\):

\[
F \, dE_{\text{app}} = -d\mu_{\text{e}} = -d\mu_{\text{e}} + F\phi = -\frac{1}{2}RT \ln n. \quad (4)
\]

Note that the relation between the chemical potentials of \(V_{\text{O}}^{\bullet\bullet}\) and \(O^{2-}\) can be easily obtained through the following internal equilibrium: \(O^{2-} + V_{\text{O}}^{\bullet\bullet} = O_2^0\).

1.2. Objective of the present study

The discussion above leads to the conclusion that under the presence of ionic conductivity, as depicted in figure 1(b), \(\mu_{\text{e}}\) in GDC varies according to the applied voltage due to the solid-state electrochemical polarization or, in other words, redox reaction caused by ion migration [17, 18]. The variation of \(\mu_{\text{e}}\) is the quantitative measure of the redox state, which is a specific feature of ion-conducting systems in comparison with semiconducting systems. The electrochemical polarization by ion migration leads to the variation of oxygen activity by oxygen non-stoichiometry and the resultant: the so-called concentration overpotential, by the variation of \(\mu_{\text{e}}\). Thus, \(\mu_{\text{e}}\) or the relative location of the Fermi level \((E_F)\) in the band gap region can be an excellent characteristic index for the detection and analysis of ionic behavior at the hetero-interface. In this study, GDC as a typical oxide-ion conducting medium is chosen to investigate the local redox reaction by an ion migration under a much simpler situation than actual switching devices in which a multiple-ion conductivity, including heterogeneous metal cation from electrodes, proton and so on, prevails. Note that the redox behavior, experimentally observed in the present study, is closely related to the resistivity switching phenomenon and is analyzed based on the present in situ measurements to understand the role of local ion migration in nano-space.

Conventional electrochemical measurements only provide the difference of \(\mu_{\text{e}}\) between the metal electrodes, as voltage and net electronic current across the metal electrodes are measurable, whereas none of the direct information related to the variation of \(\mu_{\text{e}}\) can be obtained. In this study, we employed a novel experimental method to probe the modulation of \(E_F\), induced by an electrochemical polarization at the metal/GDC heterointerface under applied dc bias using hard x-ray photoemission spectroscopy (HX-PES), which collects information from a depth of 10–20 nm [19] with a superior energy resolution compared to other methods.
such as spatial-resolve soft x-ray photoemission spectroscopy (SR-XPS) [20]. Soft x-ray absorption spectroscopy (SX-XAS) is also used to investigate the variation of Ce oxidation state caused by the electrochemical polarization to observe the very deep regime of GDC around 110 nm from the surface.

2. Experimental

2.1. Sample preparation

MIM-type cells comprising layered thin films were fabricated on a silicon substrate by RF sputtering. A 300 nm thick GDC thin film was deposited onto a platinum bottom counter electrode (BCE) on a silicon substrate by a reaction sputtering method using a sintered 20% GDC target pellet with 99.9% purity (Koujundo Chemical Laboratory Co. Ltd, Saitama, Japan) under a supply of 70 vol% Ar + 30 vol% O2 gas mixture as a reaction gas at a fixed total flow rate of 20 sccm. In all the sputtering processes, the substrate temperature was kept at room temperature. After sputtering the GDC film, the sample was annealed at 500 °C for 3 h in air primarily for crystallization and densification, in addition to water desorption to eliminate possible contribution of proton conduction. The top working electrode (TWE) was deposited to the dimensions of 3 × 3 mm2 with a thickness of 8 nm in total (schematically shown in figure 2(a)).

In the Raman scattering spectrum shown in figure 2(b), a sharp and slightly asymmetric peak A at 470 cm−1 and the doublet peaks B are attributed to the F2g symmetric breathing mode of CeO8 hexahedra and the band originated from oxygen vacancies [21, 22], respectively. These Raman peaks indicate, in contrast to very weak x-ray diffraction (XRD) peaks, comparably low crystallinity of the GDC thin film, suggesting a local coordination structure similar to the bulk crystal is readily formed. Figure 2(c) shows a scanning electron microscopy (SEM) image of the GDC thin film, indicating a dense polycrystalline film with granular morphology with grain size of few tens of nm. Figure 2(d) shows Raman scattering spectrum of the C electrode, in which structure A at 1590 cm−1 is attributed to the carbon G-band that corresponds to the symmetric stretching mode of a six-membered carbon ring [22], indicating the formation of low crystallinity graphite with an amorphous structure. Peak B at 1300 cm−1 is attributed to the D-band for a defect mode of symmetric stretching of the six-membered ring [23], further confirming low crystallinity of the C electrode.

2.2. HX-PES and SX-XAS measurement and field emission scanning electron microscopy observation

HX-PES measurements were made at the beam line BL-15XU of the SPring-8 synchrotron radiation facility in Japan. The overall resolution of the instrument estimated was 0.15 eV at 5950.2 eV of photon energy and the BE values were referenced to the metallic Au Fermi edge. In the measurement, TWEs of the cell and photoelectron spectrometer were grounded to avoid surface electrical potential variation by the external voltage applied. The present measurements were made using the excitation by hard x-ray source at a shallow incident angle of 84°, which can...
penetrate to micrometer-range depth, and the detection of photoelectrons with an escape depth of 10–20 nm. Such in situ polarization measurements have been successfully made using SR-XPS [20]. The present method provides an accurate observation of fine $E_p$ modulation by observing a chemical shift of the core level at a fixed average information depth. No in-plane two-dimensional spatial information is available by the present method. A depth profiling commonly made by an angular-dependent PES is not practical with respect to the sampling time scale of measurements for the present in situ polarization experiments. One of the advantages of the present method is that the energy resolution of the chemical shift measured is much more accurate than SR-XPS, which is appropriate to obtain direct evidence of the $E_p$ modification by ion migration.

The SX-XAS measurements were made at the beam line BL-19B in the photon factory synchrotron radiation facility in KEK, Japan. The absorption spectra were obtained by the total fluorescence yield (TFY) method. The photon energy of the experiments was referenced to the Au 4f core level of the metallic Au. All spectra were measured at room temperature under applied dc bias. Both the HX-PES and SX-XAS measurements were made after the attainment of steady state, typically waiting at least for 5 min after the dc bias voltage was applied or varied. The direction of the polarization is expressed as positive when the TWE is positively (anodically) polarized. In HX-PES measurement, probe depth is limited by an inelastic mean free path of a photoelectron, which is estimated to be 10–20 nm [19]. On the other hand, in the SX-XAS measurement by the TFY method, the probe depth is limited by x-ray attenuation length estimated to be 110 nm [24]. In the analysis of HX-PES spectra, the best fit to the experimental data of Ce3d and O1s core levels was made by the least-square fitting method under the assumption of the Voigt function as the fitting peak profile.

The GDC thin film, prepared in the same manner as the cell shown in figure 2(a), was cleaved for cross-sectional observations by thermal field emission scanning electron microscopy (FE-SEM; JSM-7001F, JEOL) at an acceleration voltage of 5 kV and a working distance of 10.0 nm.

3. Results and discussion

3.1. Electrochemical measurement

When an external voltage is applied to the present Hebb–Wagner-type asymmetric cell with the combination of reversible and BKEs, the $t_{\text{O}^\text{-}}$ value can be estimated using the current interruption method by evaluating $dE_{\text{open}}/dE_{\text{app}}$. Here, $E_{\text{app}}$ and $E_{\text{open}}$ are the applied bias and open-circuit voltage (OCV) measured immediately after interrupting a steady-state current, as superimposed in figure 3(a), showing the time variation of current and voltage across the TWE and BCE as well as the schematics of the relation between $E_{\text{app}}$ and $E_{\text{open}}$. Figure 3(a) shows the results of the current-interruption measurements made at room temperature, indicating strong asymmetric characteristics of $E_{\text{open}}$ to the polarization direction. Under cathodic polarization conditions of the TWE, $E_{\text{open}}$ follows the line for $t_{\text{O}^\text{-}} = 1$, indicating that GDC is a pure ionic conductor in this polarization condition, but starts to deviate from the line above $E_{\text{app}} = 2$ V to saturate at $E_{\text{open}} = 3.2$ V at $E_{\text{app}} > 4$ V. On the other hand, the anodic polarization of the TWE suddenly breaks down at $E_{\text{app}} > 1.1$ V. The saturated value of $E_{\text{open}} = 3.2$ V agrees well with the extrapolated voltage for the ionic conductivity predominant domain (ionic domain, hereafter) window, defined as $E_{\text{win}} = E_+ - E_-$, which can be expressed using equation (3) as

$$E_{\text{win}} = E_+ - E_- = \frac{RT}{4F} \ln \frac{P_+}{P_-}.$$

$P_+$ and $P_-$ corresponds to the oxygen activities at which the partial conductivity of holes and electrons are equal to the partial ionic conductivity, respectively. $E_+$ and $E_-$ are defined as the Nernst EMFs of the oxygen concentration cell composed of $P_{O_2} = 1.0$, as $E_+ = \frac{RT}{4F} \ln P_+$ and $E_- = \frac{RT}{4F} \ln P_-$, respectively.

Let us consider the case in which $E_{\text{app}}$ far beyond $E_{\text{win}}$ is applied. In such a case, the anode and cathode are polarized to such respective extreme oxygen activity to satisfy the Nernst equation as shown in equation (3), but GDC can only retain $E_{\text{win}}$ upon current interruption [25, 26]. As the transference number of electronic defects beyond the ionic domain is much greater than the ionic one, the excess voltage, $E_{\text{app}} - E_{\text{win}}$, is consumed by the electrical potential difference that appears as IR drop, which immediately disappears and falls back to $E_{\text{win}}$. Consequently, the OCV of 3.2 V upon negative voltage larger than $E_{\text{win}}$ is maintained at $E_{\text{app}}$. The value of $E_{\text{win}}$ is little larger than the electrolytic region of GDC, at which the transport number of the oxide ion is equal to 0.99. The value of 3.2 V is in good agreement with the value of $E_+ - E_-$, extrapolated from high-temperature data [13–16].

In the range of applied voltage from 0 to ~2 V, a large transient current observed before achieving a steady state corresponds to the oxide-ion current with a small variation of oxygen vacancy concentration, because GDC is estimated as being in the extrinsic defect regime governed by the dopant. Under a condition of large negative dc bias voltage applied, electronic conductivity prevails at the TWE side by an increased oxygen vacancy compensated by electrons, suggesting that the defect chemical situation has changed to an intrinsic defect dominant regime.

The steady-state $I$–$V$ curve in figure 3(b) also shows asymmetric feature against the polarization direction. The fact that a sudden current jump by more than one order of magnitude at $E_{\text{app}} > +1.1$ V agrees well with the breakdown voltage in the current interruption measurements suggests a possible formation of conductive path across the electrodes by the applied voltage as discussed in the following section.

In the steady-state polarization, cathodic and anodic half-cell reactions at the TWE are identical, but with the opposite directions as follows:

$$\text{O}_2^- \leftrightarrow 2e^- + V_0^{\bullet\bullet} + \frac{1}{2} \text{O}_2. \quad (B)$$
Figure 3. (a) Plot of the OCV, $E_{\text{open}}$, as a function of the applied voltage, $E_{\text{appl}}$, obtained by current interruption measurements, in which a steady-state current under galvanostatic polarization condition is suddenly shut off at time zero, as shown in the superimposed upper column, to estimate $E_{\text{open}}$ by evaluating the IR drop value. With an increase of negative bias voltage, the slope of $E_{\text{open}} - E_{\text{appl}}$ plot gradually decreases from unity to zero, whereas $E_{\text{open}}$ shows a steep decrease at a small positive voltage of $\approx 1.1$ V. (b) $I$–$V$ characteristics of Au/C/GDC (300 nm)/Pt cell obtained by a steady-state polarization and (c) the resistivity switching of the cell between HRS and LRS under a constant current ($i_{\text{ext}} = 100$ nA) and open-circuit condition ($i_{\text{ext}} = 0$ nA). First, the cell is polarized by constant current mode with an external current of 100 nA. After 5 s, the potential difference of the two electrodes shows an abrupt drop to a very small value due to HRS to LRS transition. The external current was then switched to 0 nA and kept for 4 h. Subsequently, the resistivity of the cell, measured under a constant current of 100 nA, recovered to an original value of several tenth mega ohms, corresponding to the LRS to HRS transition.

On the other hand, cathodic and anodic half cell reaction at the BCE is described by the following reactions:

\[ \text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+} \]  
\[ \text{O}_2^- + h^+ \rightarrow O_2 \]  

(C) \hspace{1cm} (D)

Note that, after the anodic polarization of the TWE for a long period of time or at a large current density, electronic conduction becomes predominant, while GDC near the TWE has been polarized to the oxidation direction. Such a resistivity jump that appears even at a comparably small positive bias voltage of about 1 V, as indicated by the green arrow in figure 3(b), can be interpreted as a reduction of almost the entire GDC film by the combination of oxygen evolution from the TWE to a gas phase (reaction (B)) and reduction of Ce$^{4+}$ to Ce$^{3+}$ (reaction (C)) by a net $V_{\text{O}}^+$ transport from the BCE to the TWE.

We propose here a model assuming the presence of moving reduction front with $P_{\text{O}_2} = P_- (P_-$ front) of reduced domain, which proceeds from cathode side (BCE) to anode side (TWE) in solid electrolytes, as suggested for yttria-stabilized zirconia and doped SrTiO$_3$ at high temperatures [27, 28]. Finally, the $P_-$ front approaches TWE with an extremely thin oxidized skin layer, which breaks down due to the strong applied electrical field to form a conductive path to electronically connect the two electrodes. This is closely related to the resistivity switching phenomenon from the high resistivity state (HRS) to low resistivity state (LRS), in terms of resistivity variation by electrochemical reduction, reported in pure CeO$_2$ [29, 30] and other various oxide thin films [1–4].

Figure 3(c) shows the resistivity switching of the cell by oxygen evolution under a constant current condition ($i_{\text{ext}} = 100$ nA). The switching from HRS to LRS observed as a sudden resistivity jump by one to two orders of magnitude is observed at 5 s after the constant current is applied, followed by a wide irregular serration of resistivity. Subsequently, by keeping an open-circuit condition ($i_{\text{ext}} = 0$ nA) for 4 h, the cell shows full recovery from LRS to HRS by the oxide ion migration. Therefore, the present switching mode can be classified as a volatile or semi-volatile switching, caused by a fast re-oxidation of the GDC film (reaction (B)).

The fact that the switching occurs at such a small dc bias voltage possibly originates from the fast oxide ion migration to reduce the oxidized layer thickness for rapid increase of electrical potential gradient, leading to an easy formation of...
the filament-like reduced defect filament, which consists of Ce\(^{3+}\), presumably at the grain boundary of the GDC film.

3.2. Hard x-ray photoemission spectroscopy

Figures 4(a) and (b) show the PES spectra for the Ce3d (Ce3d\(^{3/2}\) and Ce3d\(^{5/2}\)) and O1s core levels of GDC at the TWE/GDC interface under dc-bias applied conditions, respectively. Basically, both the core-level spectra show a simple parallel chemical shift of the Ce3d and O1s orbital upon bias voltage application, but with noticeable peak broadening under conditions of large anodic bias (positive) voltage applied, suggesting a steep band bending in GDC near the TWE as explained later in figure 5(c). The Ce3d spectra show a multiplet structure, corresponding to three final states with 3d\(^9\)4f\(^0\), 3d\(^9\)4f\(^1\) and 3d\(^9\)4f\(^2\)\(^L\) configurations for both 3d\(^{3/2}\) and 3d\(^{5/2}\). The 3d\(^9\)4f\(^2\)\(^L\) configuration is caused by the charge transfer from the O2p to Ce4f orbital, due to lowered energy level by a strong electrostatic core–hole interaction [31, 32]. Additional satellite peaks, indicated by arrows A–C, that appear in negatively biased conditions, represent the Ce\(^{3+}\) state [33] originating from strong screening of the core–hole interaction and the resultant decrease in the excitation energy of photoelectrons from each core level by the increase in screening Ce4f electrons.

The binding energies (BEs) of O1s and Ce3d\(^{3/2}\) for the 3d\(^9\)4f\(^0\) final state (indicated by D in figure 4(a)), plotted against the applied bias voltage in figure 4(c), exhibit sigmoidal-shaped parallel variations between the reduction and oxidation limits. The parallel shift observed indicates a fixed BE difference of about 387.7 eV between these two core
Figure 5. Stack plots of Ce $M_4$- and $M_5$-XAS spectra under (a) negative and (b) positive bias voltage conditions applied to the TWE. Peaks A$'$, B$'$ and C$'$ in $M_4$ spectra are attributed to peaks A, B and C in $M_5$ spectra. (c) Variation of A/C peak ratio with applied negative (blue) and positive (red) bias voltage, indicating an anomalous reduction upon application of large positive bias voltage due to the net oxygen loss from the TWE and resultant GDC film reduction. For the analysis of the A/C peak ratio, the peak intensities at 879.0 and 886.4 eV of photon energy, which correspond to structure A and C, are estimated by subtracting background and then the A/C peak ratio is calculated. (d) A cross-sectional FE-SEM image of the cell after O$_2$ evolution from the BCE upon application of $-24$ V.

levels of Ce3d and O1s, suggesting a rigid-band behavior in which only $E_F$ shifts within the redox window without any secondary effect. Such $E_F$ shift behavior under applied dc-bias voltage conditions clearly evidences a variation of $\mu_e$ caused by the redox reaction driven by the oxide ion migration. The redox window ($E_{\text{win}}$) of the GDC film under the applied voltage conditions, estimated as $E_{\text{win}} \approx 3.2$ eV, is identical to the apparent band gap width of 3.2 eV as shown in figure 4(d), measured by UV–Vis absorption spectroscopy, the value of which is in good agreement with reported ones [29].

The emergence of the Ce$^{3+}$ satellites at the lower BE side of the Ce3d core levels accompanied by the saturation of the chemical shift of $E_F$ toward the conduction band is clear and consistent evidence for the occurrence of electrochemical reduction at the TWE/GDC interface and pinning at the Ce$^{3+}$ donor state (Ce4f donor level) due to its large donor density of states (DOS), as observed in figures 4(a) and (c). On the other hand, the origin of the oxidation limit is attributed to the pinning of $E_F$ by the acceptor level, corresponding to the O$^{\cdot-}$ state: unoccupied localized O2p orbital. The redox behavior of the GDC thin film and its relation to oxygen evolution can be explained from a hysteretic feature of BE shifts of Ce3d and O1s core levels as follows.

Within a small bias voltage range to both cathodic and anodic directions, BEs of the Ce3d and O1s core level show reversible shift (purple symbols in figure 4(c)), while BEs at the OCV condition (A in figure 4(c)) after applying a large positive bias voltage to the TWE have shifted irreversibly by 700 meV to the higher BE side (reduction side) shown by point B. This polarization corresponds to the break down condition shown in figures 3(a) and (b) for anodic polarization. Although GDC near the TWE undergoes an
intensive anodic (oxidative) polarization, the Ce\textsuperscript{3+}-related peaks indicated as A, B and C in figure 4(a), which signify the reduction of GDC, appear even at OCV condition after applying a large positive bias voltage in HX-PES. These apparent inconsistent results can be well explained by assuming the electrochemical reduction of the entire GDC film due to O\textsubscript{2} evolution at the TWE except for a very thin skin layer in contact with the TWE left oxidized, while the TWE virtually serves as a blocking or semi-BkE under negative and small positive bias voltage conditions. The blocking nature is lost when a large positive bias voltage is applied to the TWE, and the cell starts to function similar to a Hebb–Wagner-type asymmetric cell with a combination of reversible (oxygen-releasable) TWE and blocking platinum BCE. The reaction (B) proceeds to the right-hand side at the TWE, while the reaction (C) proceeds at the BCE and both \( V_{\text{3+}}^\bullet \) and \( e^- (\text{Ce}^{3+}) \) are formed at the TWE under an intense anodic polarization, resulting in the net reduction of GDC film. As shown in figure 4(c), by green horizontal arrows, the slope of chemical shift under large positive bias voltage becomes much gentler than those under small positive and negative bias conditions. Upon interrupting the polarization, the charged ionic defects can be immediately redistributed along their own chemical potential, because the increased partial electronic conductivity now becomes predominant by overriding the partial oxide ion conductivity.

Relaxation behaviors of the chemical shifts before and after O\textsubscript{2} evolution from the TWE are shown in figure 4(e). The measurement before O\textsubscript{2} evolution from the TWE has been made by applying the bias voltage of \(-5\, \text{V}\) (point C in figure 4(c)) to the TWE for 20 min followed by switching to 0 V at time zero in figure 4(e), showing a slow relaxation to the initial state. On the other hand, the measurements after O\textsubscript{2} evolution from the TWE by applying the large dc bias voltage of \(-14\, \text{V}\) (point D in figure 4(c)) for 20 min followed by switching to 0 V at time zero show no relaxation due to a uniform potential profile in the entirely reduced bulk of GDC. These TWE-relaxation behaviors (A) before and (B) after, shown in figure 4(e), are totally different, clearly indicating the effect of the net GDC film reduction: before O\textsubscript{2} evolution, the relaxation upon interrupting cathodic polarization occurs within GDC by the redistribution of \( V_{\text{3+}}^\bullet \) and \( e^- \), both of which have been localized to the TWE side by a concentration polarization in GDC. The kinetics is governed by the partial conductivity of the second fastest carrier, either electrons or holes, leading to slow relaxation despite the fast partial oxide ion conduction due to slow migration of electronic carriers as GDC is in the ionic domain. On the other hand, after an irreversible GDC reduction by the O\textsubscript{2} evolution from the TWE, the electronic conductivity dominates over the oxide ion conductivity in the bulk GDC film, and therefore the steady state is immediately attained upon interrupting the cathodic polarization (figure 4(e)).

3.3. Soft x-ray absorption spectroscopy

The Ce\text{M\_4-} and \text{M\_5-XAS} spectra under bias voltage-applied conditions are shown in figures 5(a) and (b). Both Ce\text{M\_4-} and \text{M\_5-XAS} spectra are known to have two peaks, corresponding to the final state of 3d\textsuperscript{4}f\textsuperscript{4} and 3d\textsuperscript{4}f\textsuperscript{2}L\textsuperscript{2} configuration for Ce\textsuperscript{4+} [34, 35]. The initial state of Ce\textsuperscript{3+} is 3d\textsuperscript{4}f\textsuperscript{2} which exhibits similar multiplet structure in HX-PES spectra, while the absorption energy is about 2 eV lower than the Ce\textsuperscript{4+} state due to a stronger screening effect by Ce4f electrons [36]. Consequently, both CeM\textsubscript{4-} and M\textsubscript{5-XAS} spectra of CeO\textsubscript{2} in a mixed valence state are convolutions of the two spectra of Ce\textsuperscript{3+} and Ce\textsuperscript{4+}. Peaks A and C are ascribed to Ce\textsuperscript{3+} and Ce\textsuperscript{4+} states, respectively, and peak B includes these two contributions. In order to estimate the Ce oxidation state, the intensity ratio of peak A to C is plotted as a function of applied bias voltage in figure 5(c). Under negative bias (cathodic polarization) conditions, the A/C peak ratio is almost constant when \( E_{\text{app}} > -3\, \text{V} \). Further increase of negative bias voltage results in a considerable increase of the A/C peak ratio, indicating the occurrence of electrochemical reduction due to the increase of \( V_{\text{3+}}^\bullet \) at the TWE/GDC interface (see figure 6(a)). On the other hand, when a positive bias voltage is applied to the TWE, the A/C ratio slightly decreases upon the increase of \( E_{\text{app}} \) from 0 to 5 V by an electrochemical oxidation of GDC near the TWE as shown in figures 6(b) and (c). When the positive bias voltage is further increased above 5 V, the A/C peak ratio suddenly turns into a rapid increase similar to the case of negative bias applied conditions, suggesting an increase of Ce\textsuperscript{3+} density in the probed depth region.

Under relatively small positive bias, the TWE serves as a BkE, and a reversible electrochemical oxidation of GDC near the TWE takes place (see figure 6(b)) as discussed above. Upon increased positive bias voltage, both O\textsubscript{2} evolution at the TWE and the reduction of GDC at the BCE occur, resulting in the formation of a deeply reduced GDC domain that expands from the BCE toward the TWE side. A low electrical potential gradient in the reduced domain due to an enhanced electronic conductivity results in a low oxygen chemical potential gradient. Finally, an extremely thin oxidized skin layer, formed near the TWE, sustains the majority of the applied electrical potential. Due to the large SX-XAS information depth of \(~110\, \text{nm}\), the observed SX-XAS spectra mainly reflect the reduced domains far below the \( P_- \) front, while HX-PES probes only the oxidized skin layer due to its extremely shallow information depth of \(~10–20\, \text{nm}\) (see figure 6(c)). Accordingly, the increase in the A/C peak ratio above 5 V is attributed to the bulk GDC reduction by the O\textsubscript{2} evolution from the TWE, probably due to the easy escape ability of O\textsubscript{2} gas to the surrounding vacuum from the TWE due to its porous morphology. In contrast to the positive bias applied condition, O\textsubscript{2} gas evolution from the BCE to vacuum under negative bias application to the TWE is suppressed due to extremely slow kinetics of charge transfer reaction as well as gas tight structure at the BCE/GDC interface, while further application of intense negative bias voltage causes a vigorous precipitation of O\textsubscript{2} gas at the BCE to lift off the GDC film to form blisters, as shown in figure 5(d).

3.4. Discussion on the electrochemical polarization

Figure 6 shows schematic illustrations of the electrochemical polarization, expressed as the Fermi energy profile across the
Figure 6. Schematic illustrations (the figures on the left-hand side show the profile under applied bias voltage condition and those on the right show the profile just after the current interruption) of the Fermi energy profile, estimated from the present electrochemical polarization experiments, under the assumptions of the reversible electrochemical polarization and the irreversible O₂ gas evolution: (a) when negative bias voltage is applied to the TWE, (b) when positive bias voltage is applied to the TWE up to 5 V and (c) up to above 10 V. Red, blue and black solid lines indicate $E_+, E_-$ and potential profile inside the GDC thin film, respectively. For simplification, the profile of an electrostatic field inside GDC is assumed as linear, whereas local conductivity modulation, caused by both ion blocking and contribution of electronic conductivity, due to resultant p–n transition, makes the profile of electrostatic field nonlinear. In the case of (c), after dc bias is removed, $E_{\text{open}}$ immediately becomes zero due to short circuit of the thin oxidized layer in the vicinity of the TWE due to needle-like defects (indicated by gray pillars) that penetrates from reduction front to the TWE.
GDC electrolyte under steady-state polarization, and just after the current interruption. When a steady state is attained under negative bias voltage application to the TWE, no reaction takes place at the BCE due to the complete blocking situation followed by the reduction of GDC near the TWE. If $E_{\text{app}}$ is larger than $E_{\text{win}}$, $E_{\text{app}}$ is distributed to satisfy the following equation, if overpotential at the electrodes are neglected:

$$E_{\text{app}} = E_{\text{win}} + \Delta \phi.$$  

The second term, $\Delta \phi$, corresponds to the electrical potential difference of GDC in contact with the TWE and BCE, and governs the electronic and ionic transport under applied bias voltage conditions. Within the redox window, the band bends due to both p–n transition and $\mu_{e'}$ variation in GDC under the condition where ionic current is suppressed. No overpotential, defined as the Fermi energy gap between an electrode and GDC, builds up under the condition, in which no charge transfer reaction takes place. It is reasonable to assume an extremely short relaxation time for the attainment of local equilibrium for electrons. This is evidenced by the fact that no $\tilde{\mu}_{e'}$ gap at the interface is observed in HX-PES measurements. Instead, a gap in $\mu_{O_2}$ is estimated to occur between the electrode/GDC interface to satisfy the local equilibrium expressed by reaction (B). After the current interruption, the electrical potential in the special region beyond the redox window immediately relaxes and falls back to generate $E_{\text{win}}$ as an OCV when measured after the current interruption, as shown in figure 6(a). This $E_{\text{win}}$ is alternatively defined as diffusion potential formed by oxide ion migration and resultant oxygen chemical potential profile. Note that the GDC survives in such surprisingly high oxygen chemical potential conditions, which is calculated as $\approx 10^{30}$ bar [37].

On the other hand, when a positive bias voltage is applied to the TWE, the $O_2$ gas evolution reaction takes place at around ambient total pressure, and the BCE side is cathodically polarized with reference to a partially reversible electrode maintained approximately at ambient $O_2$ gas pressure. When it is further polarized, as shown in figure 6(c), GDC at the BCE side is further reduced and the reduced $P_-$ front proceeds to the vicinity of the TWE to enlarge the n-type domain. Finally, owing to the formation of an extremely steep electrical potential gradient, the oxidizing skin layer is short circuited by a conductive filament formation possibly along the grain boundary, as described in the preceding section.

The slow kinetics of electrode reactions prevent net ion migration and resultant oxygen gas formation taking place until a certain critical electrical voltage is exerted, as schematically illustrated in figure 7. Therefore, the authors propose a possibility that eventually small net motive force is present for neutral oxygen transport between two electrodes, but a strong motive force for the ion migration within GDC remains to propagate when increased applied voltage exceeds a critical value for the precipitation of $O_2$ gas. Since all the cells used are MIM-type two-electrode cells, where the reference/counter electrode is not an ideal non-polarizable electrode, we are not able to define overpotential at each electrode/electrolyte interface from the present measurements. In addition, a situation strongly influenced by the kinetic aspect of electron transfer across GDC, such as a small possibility of barrier formation at the interface, and Poole–Frenkel electron transport and so on, contributes to the increased complexity of the potential profile, but easy electrons transfer across the interface in comparison to such extremely sluggish ion transport across the GDC/electrode interface may maintain the equality of $\tilde{\mu}_{e'}$.

What we could measure by conventional electrochemical measurement was merely the electrochemical potential difference between the metal electrodes and the net electronic current through a metal electrode monitor as external current. It is novel to find that the present in situ measurements using HX-PES and SX-XAS can provide direct evidence of $E_F$ modification by ion migration. The authors note that direct evidence of such local polarization near the contacting electrode by ion migration in an electrolyte is obtained through a novel approach using modern in situ HX-PES and SX-XAS measurements in this study.

4. Conclusion

The redox reaction by the oxide ion migration at the TWE/GDC heterointerface has been successfully observed using HX-PES and SX-XAS techniques. The $E_F$ level at the TWE/GDC interface shows a reversible variation within the apparent redox window of 3.2 eV, which is equal to the redox window of $E_{\text{win}} = E_a - E_e$, identical to the apparent band gap energy between acceptor and donor levels. The redox window is limited by the pinning at large DOS of Ce$^{3+}$/Ce$^{4+}$ donor level as the reduction limit and the acceptor level as the oxidation limit, which corresponds to $E_+$ and $E_-$, respectively. The reversible redox reaction takes place under the closed system condition in which no mass is transferred from the cell, while an irreversible reduction of the GDC film is observed due to $O_2$ evolution to the surrounding gas phase. The present results indicate direct evidence of ion migration and resultant concentration polarization of
electrolyte in the vicinity of the electrode area at the nm scale. Surprisingly, applied voltage is quickly relaxed by ion migration and the electrode reaction proceeds even at this low temperature under intense polarized conditions. The authors note that, even at the nm scale, a macroscopic solid-state ionic principle holds and $E_F$ is an excellent index to understand the redox status of oxides. Finally, the present approach using HX-PES and SX-XAS, applicable to many other solid-state electrochemical devices, such as ReRAM, electrochemical metallization devices, Li ion batteries, electrochemical capacitors and so on, may be a powerful tool to investigate such local electrochemical polarization for better fundamental understanding of ionic phenomena in solid-state ionic materials.

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