First observation of surface protonics on SrZrO₃ perovskite under a H₂ atmosphere†

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This is the first direct observation that surface proton hopping occurs on SrZrO₃ perovskite even under a H₂ (i.e. dry) atmosphere. Understanding proton conduction mechanisms on ceramic surfaces under a H₂ atmosphere is necessary to investigate the role of proton hopping on the surface of heterogeneous catalysts in an electric field. In this work, surface protonics was investigated using electrochemical impedance spectroscopy (EIS). To extract the surface proton conduction, two pellets of different relative densities were prepared: a porous sample (R.D. = 60%) and a dense sample (R.D. = 90%). Comparison of conductivities with and without H₂ revealed that only the porous sample showed a decrease in the apparent activation energy of conductivity by supplying H₂. H/D isotope exchange tests revealed that the surface proton is the dominant conductive species over the porous sample with H₂ supply. Such identification of a dominant conductive carrier facilitates consideration of the role of surface protonics in chemical reactions.

Surface protonics is recognized as proton transportation on an oxide surface in a middle-temperature or low-temperature region. In a H₂O atmosphere, protons are transferred continuously between M–OH₂ and M–OH⁻ formed by supplied H₂O by the Grotthuss mechanism. Investigation of surface protonics is anticipated to yield useful knowledge for application to various electrochemical devices such as fuel cells, chemical sensors, and electrolyzers. Recently, an important role of surface protonics during heterogeneous catalytic reactions was found in an electric field under both H₂O and H₂ atmospheres. It promotes low-temperature catalysis for hydrogen production, ammonia synthesis, and other processes. Electrochemical impedance spectroscopy (EIS) of oxide surfaces under a H₂O atmosphere has been investigated to elucidate the correlation between catalysis in an electric field and surface protonics (Scheme 1). The results show a good agreement between the H₂O partial pressure dependence on surface protonics and that on catalytic activity in the electric field. The correlation revealed the strong contribution of surface protonics to the enhanced reaction rate at a low temperature in the electric field. Therefore, EIS measurements is a promising method for the evaluation of surface protonics during catalytic reaction with an electric field.

This study provides the first example of the observation of surface protonics under a H₂ atmosphere (i.e. in a dry condition) using EIS measurements. As the sample, SrZrO₃, which was used for ammonia synthesis in the electric field, was selected. Measurements were performed with porous (relative density, R.D. = 60%) and dense (R.D. = 90%) SrZrO₃ pellets. Earlier reports have described that porous pellets that have low relative density (R.D. = 50–60%) are feasible for extracting surface conductive components because many more vacant sites exist for adsorbate species to adsorb on the oxide surface than on dense pellets (R.D. > 90%). Surface protonics was confirmed from comparison of the respective behaviors of porous and dense samples.

We prepared two types of SrZrO₃ pellets having low (60%) and high (90%) densities. SrZrO₃ powders were synthesized using a complex polymerization method. Then porous and dense SrZrO₃ pellets were prepared. The detailed preparation method...
is described in the ESI. All electrochemical impedance spectroscopy (EIS) measurements were taken in a measurement cell (ProboStat™, NORECS AS, Norway) using a two-electrode four-wire setup connected to an impedance spectrometer (alpha-A; Novocontrol Technologies) with a ZG4 interface. The impedance spectra were recorded at frequencies of 10^6–10^-3 Hz using an oscillation amplitude of 100 mV RMS (root mean square). Temperature dependences of electrochemical conductivity were examined under a N2 atmosphere at 423–723 K and under N2 + H2 atmospheres at 348–723 K. Impedance data were analyzed using ZView equivalent circuit fitting software (ver. 3.5a; Scribner Associates Inc.) using a [RC][RC]Cstray equivalent circuit model, as presented in Fig. S1 (ESI†). The (RC) components were assigned to the series-connected bulk and grain boundary transport. Also, Cstray denotes parallel-connected parasitic capacitance. The values of electrochemical conductivity (σ) were calculated for both the bulk (b) and grain boundary (gb) using eqn (1). In this equation, L represents the pellet thickness, S denotes the area of the Pt electrode, and R stands for the fitted resistance value. The apparent activation energy (Ea) of the electrochemical conductivity was calculated for both the bulk and grain boundary using the Arrhenius expression. For eqn (2), where A shows the pre-exponential, kB denotes Boltzmann’s constant.

\[
\sigma_x = \frac{L}{SR_x} \quad (x = b, gb) \tag{1}
\]

\[
\sigma_T = A \exp(-E_a/k_B T) \tag{2}
\]

X-ray photoelectron spectroscopy (XPS) measurements (Versa Probe II; Ulvac-Phi Inc.) were carried out with an Al Kα X-ray source. The binding energies were calibrated using the C1s peak to 284.8 eV.26,27 The pre-treatment conditions were classified into 3 patterns: (A) N2 purge at 723 K for 2 h, (B) H2 reduction under a N2 + H2 atmosphere at 723 K for 2 h, and (C) N2 purge for 2 h after H2 reduction at 723 K for 2 h.

The crystalline phases for the synthesized SrZrO3 powder and pellets were evaluated from XRD measurements. As presented in Fig. S2 (ESI†), all samples have an orthorhombic perovskite structure. The binding energies of both the porous and dense pellets were assessed using FE-SEM, as depicted in Fig. 1. Numerous pores were detected in the porous pellet. Such a porous sample is extremely useful for the detection of surface conductions induced by the adsorbed H2O on the grain surface at low temperatures under H2O conditions.4,5,20–25

To evaluate the relative density dependence of electrochemical conductivity, EIS measurements were conducted under N2 or N2 + H2 atmospheres using porous (R.D. = 60%) and dense (R.D. = 90%) SrZrO3 samples. Fig. 2 depicts the temperature dependence of electrochemical conductivity on each sample. Fig. 3 presents the Nyquist plot for each sample under N2 and N2 + H2 atmospheres at 723 K. Accordingly, the porous sample and dense sample exhibited completely different trends. Regarding the result of the porous sample (Fig. 2(A)), the electrochemical conductivity of both the bulk and grain boundary under a N2 atmosphere decreased along with decreasing temperature, exhibiting typical Arrhenius behavior. The apparent activation energies of electrochemical conductivity were calculated as 0.93 eV and 0.89 eV, respectively, for the bulk and grain boundary. When H2 was supplied, the apparent activation energy of the electrochemical conductivity decreased markedly compared to that under N2 atmosphere: 0.47 eV (bulk) and 0.74 eV (grain boundary). Regarding the dense sample (Fig. 2(B)), however, the temperature dependence and the apparent activation energy for the dense sample under a H2 atmosphere were identical to those under a N2 atmosphere. Such a difference between porous and dense samples might be attributable to the dissociative adsorption of the supplied H2 on the grain surface, as described in eqn (3).

\[
\text{H}_2(\text{g}) = 2\text{H}_2^+ + 2\text{e}^- \tag{3}
\]

Additionally, hydrogen partial pressure (P_H2) dependence was studied at 723 K with a porous sample to elucidate the surface proton contribution to the total conductivity under a H2 atmosphere. Before varying the partial pressure, the sample was

![Fig. 1 FE-SEM images of SrZrO3: (A) porous pellet (R.D. = 60%) and (B) dense pellet (R.D. = 90%).](image-url)
pretreated at 723 K for 2 h under a H₂ atmosphere to mitigate changes in conductivity caused by H₂ reduction. Then H₂ partial pressure was decreased to 0.1 atm. Impedance measurement was carried out for two plots (P₁ = 10⁻⁵ and 1 atm) with increasing order, then the measurement was continuously performed at P₂ = 10⁻⁵ atm with decreasing order. Consequently, as shown in Fig. 4, positive dependence of H₂ partial pressure on the electrochemical conductivity was confirmed. Therefore, the dominant conductive carrier was inferred as electrons under a N₂ atmosphere and surface protons under a H₂ atmosphere for a porous sample, and as electrons under a N₂ or H₂ atmosphere for a dense sample. In addition, the former plot (red) and the latter plot (blue) at P₁ = 10⁻⁵ atm were exactly identical, indicating that the conductivity could be reproduced after removing surface protons. This result demonstrates that the coverage of surface OH⁻ groups is reversible with varying hydrogen partial pressure. The results of these investigations clarified that the decrease in apparent activation energy and the increase of conductivity under a H₂ atmosphere were attributed to H₂ dissociative adsorption on the grain surface, caused by the appearance of surface protons.

To ascertain whether the dominant conductive carrier on the porous sample under H₂ conditions is protons or not, H/D isotope effects were assessed with the porous and dense samples. As presented in Table 1, the porous sample exhibited an H/D isotope effect at all measured temperatures (σD/σH ≈ 0.5), indicating protons as the dominant conductive carrier. Such a significant H/D isotopic value is explainable by a semi-classical theory.28–32 Considering a potential barrier for proton (or deuteron) transfer reaction, a proton’s binding energy is (1/2)ħν_H at the zero-point vibration energy level. The difference in activation energy between a proton and deuteron can be shown as presented in eqn (4).

\[ \sigma_D/\sigma_H = \frac{\sigma_D}{\sigma_H} \]

Assuming that the wave number is derived from the OH⁻ stretching frequency, correlation can be found such as ν ∝ \( m^{-1} \), where m represents the mass of a proton or deuteron. Regarding OH⁻ ions in SrZrO₃-based oxides, the OH⁻ stretching frequency is reported as around 3650 cm⁻¹ order.34,35 Using this value, the difference of the activation energies (\( E_D - E_H \)) is calculated theoretically as 0.055 eV, and the experimental results were 0.03 eV. It is slightly lower than the theoretical value, probably because a small difference in energy level exists not only at the initial state, but also at the transition state. Considering that point, a slightly lower value would typically be obtained for the difference in the activation energies.30,31,36 Protons are formed by H₂ dissociative adsorption on the porous SrZrO₃ surface. The resulting surface proton hopping dominates conduction under a H₂ atmosphere.

As mentioned above, it is indubitable that the increase of conductivity with H₂ addition is attributed to surface proton conduction. It is also important to assess the change of oxidation state by H₂ reduction. Therefore, XPS measurements were performed with SrZrO₃ samples which were pre-treated with various conditions: (A) N₂ purge, (B) H₂ reduction, (C) N₂ purge after H₂ reduction. Fig. 5 presents O1s XPS spectra. As a result, two peaks at around 529 eV and 531 eV were observed for all patterns ([A]–[C]). These peaks are assigned to Oₓ or OH⁻ ions in SrZrO₃-based oxides, the OH⁻ stretching frequency, correlation can be found such as ν ∝ \( m^{-1} \), where m represents the mass of a proton or deuteron. Regarding OH⁻ ions in SrZrO₃-based oxides, the OH⁻ stretching frequency is reported as around 3650 cm⁻¹ order.34,35 Using this value, the difference of the activation energies (\( E_D - E_H \)) is calculated theoretically as 0.055 eV, and the experimental results were 0.03 eV. It is slightly lower than the theoretical value, probably because a small difference in energy level exists not only at the initial state, but also at the transition state. Considering that point, a slightly lower value would typically be obtained for the difference in the activation energies.30,31,36

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\[ E_D - E_H = \frac{1}{2}\hbar (\nu_D - \nu_H) \]

Table 1. H/D isotope effect values of porous (R.D. = 60%) and dense (R.D. = 90%) SrZrO₃ samples under H₂(D₂) atmosphere: N₂: H₂(D₂) = 1:3 gas flow, 423–723 K temperature, 60 sccm total flow rate

| Temperature/K | Porous SrZrO₃ Sample | Dense SrZrO₃ Sample |
|---------------|----------------------|---------------------|
|               | \( \sigma_H / S \text{ cm}^{-1} \) | \( \sigma_D / S \text{ cm}^{-1} \) | \( \sigma_D/\sigma_H \) | \( \sigma_H / S \text{ cm}^{-1} \) | \( \sigma_D / S \text{ cm}^{-1} \) | \( \sigma_D/\sigma_H \) |
| 723           | 1.21 × 10⁻⁷          | 7.91 × 10⁻⁸         | 0.65          | 2.43 × 10⁻⁶          | 2.41 × 10⁻⁶         | 0.99          |
| 623           | 1.70 × 10⁻⁸          | 9.88 × 10⁻⁹         | 0.58          | 4.14 × 10⁻⁷          | 4.12 × 10⁻⁷         | 1.00          |
| 523           | 5.01 × 10⁻¹⁰         | 2.62 × 10⁻¹⁰        | 0.52          | 2.57 × 10⁻⁸          | 2.55 × 10⁻⁸         | 0.99          |
| 423           | 4.74 × 10⁻¹¹         | 2.27 × 10⁻¹¹        | 0.48          | 2.44 × 10⁻¹⁰         | 2.42 × 10⁻¹⁰        | 0.99          |
formation by H₂ dissociative adsorption on the grain surface. Then proton conduction occurs under a H₂ atmosphere. H/D isotope effects indicated proton migration on the oxide surface with the hopping mechanism. Such identification of a dominant conductive carrier is an important consideration when assessing correlation between surface ion conduction and chemical reactions.

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Conflicts of interest

There are no conflicts to declare.

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