Fast and Stable Proton Conduction in Heavily Scandium-Doped Polycrystalline Barium Zirconate at Intermediate Temperatures

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The environmental benefits of fuel cells and electrolyzers have become increasingly recognized in recent years. Fuel cells and electrolyzers that can operate at intermediate temperatures (300–450 °C) require, in principle, neither the precious metal catalysts that are typically used in polymer-electrolyte membrane systems nor the costly heat-resistant alloys used in balance-of-plant components of high-temperature solid oxide electrochemical cells. These devices require an electrolyte with high ionic conductivity, typically more than 0.01 S cm$^{-1}$, and high chemical stability. To date, however, high ionic conductivities have been found in chemically unstable materials such as CsH$_2$PO$_4$, In-doped SnP$_2$O$_7$, BaH$_2$, and LaH$_3$-2O$_x$. Here, fast and stable proton conduction in 60-at% Sc-doped barium zirconate polycrystal, with a total conductivity of 0.01 S cm$^{-1}$ at 396 °C for 200 h is demonstrated. Heavy doping of Sc in barium zirconate simultaneously enhances the proton concentration, bulk proton diffusivity, specific grain boundary conductivity, and grain growth. An accelerated stability test under a highly concentrated and humidified CO$_2$ stream using in situ X-ray diffraction shows that the perovskite phase is stable over 240 h at 400 °C under 0.98 atm of CO$_2$. These results show great promises as an electrolyte in solid-state electrochemical devices operated at intermediate temperatures.

Conventional materials have challenges either in high-conductivity temperature regime or high chemical stability between 350 and 450 °C.[$^1$] CsH$_2$PO$_4$ solid acids show proton conductivity over 0.01 S cm$^{-1}$ in the temperature range of 230 to 254 °C.[2] Such materials, however, decompose above these temperatures.[$^2$] In-doped SnP$_2$O$_7$ shows proton conductivity over 0.1 S cm$^{-1}$ at slightly higher temperatures up to 300 °C.[3] The conductivity of this material, however, strongly depends on the synthesis process, making its reproducibility low.[4] The hydride ion conductors BaH$_2$[$^5$] and LaH$_3$-2O$_x$[$^6$] are another class of materials that show such conductivity, but the high reactivity of these materials make them unsuitable as electrolytes for fuel cells and electrolyzers. Within the stable oxide category, 20-at% Y-doped barium zirconate exhibits a total proton conductivity of 0.01 S cm$^{-1}$ at 450 °C.[$^7$] A further increase in the total proton conductivity is, in principle, possible by attaining larger values of proton concentration, bulk proton diffusivity, specific grain boundary conductivity, and a lower density of grain boundaries. Heavy doping of Y in barium zirconate enhances the proton concentration,[$^8$] but lowers the conductivity, with a maximum of around 20 at%.$^9$[10] Recent DFT-kinetic Monte Carlo simulations, on the contrary, predict enhanced bulk proton conductivity for the 40 at% Y-doped fully hydrated sample.[11] Choosing a dopant with a lower proton-dopant association energy would enhance the bulk proton diffusivity.$^{12,13}$ To date, however, no dopant has led to a substantial enhancement over Y.$^{14}$ Insufficient grain growth due to the refractory nature of barium zirconate creates a high density of resistive grain boundaries.$^{17}$ So far, no materials have met the desired properties at the intermediate temperatures of 300–450 °C.

We demonstrate fast and stable total proton conduction in heavily proton- and Sc-doped barium zirconate (HSBZ) polycrystal with a Sc doping level of 60 at% (60Sc) at 396 °C, Figure 1a. The material was synthesized from a chemical solution and sintered at 1600 °C for 24 h, resulting in a dense pellet with a relative density of 95%. The chemical composition analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) was Ba$_{0.91}$Zr$_{0.395}$Sc$_{0.605}$O$_3$-δ. The X-ray diffraction pattern of a dehydrated 60Sc sample showed a single perovskite phase with no indication of a secondary
phase, Figure S1a, Supporting Information. The high solubility of Sc in BaZrO₃, up to 59 at%, is consistent with the ternary BaO-ZrO₂-Sc₂O₃ phase diagram,[15] in which the extent is larger than that of Y, ≈50 at%.[16] The Rietveld refinement indicates a cubic structure. Although the ionic radius of the Sc dopant for 6 coordination (0.745 Å) is larger than 0.72 Å for Zr,[17] 60Sc showed a lattice constant of 4.16959 Å, smaller than that for undoped BaZrO₃, 4.193 Å.[18]

The cubic perovskite phase in the 60Sc sample was maintained after the hydration, although a trace amount of BaCO₃, estimated as 0.23 wt% from the Rietveld refinement, appeared, Figure S1b, Supporting Information. Thermogravimetry results showed a typical behavior of hydration, with a higher proton concentration at lower temperatures due to the negative hydration enthalpies found in the proton-conducting oxides.[19] The proton concentration in the 60Sc sample reached 0.55 mol per formula unit, which is close to the theoretical maximum of 0.6 and approximately three times higher than that of a 20-at% Sc-doped sample (20Sc), Figure S2, Supporting Information. The hydration enlarged the lattice by 1.15%. The hydration enthalpies were determined to be −96 ± 2 and −121 ± 2 kJ mol⁻¹ for 20Sc and 60Sc, respectively, considering a fact that a small amount of oxygen vacancies, 0.011 and 0.023 mol per formula unit in the 20Sc and 60Sc, respectively, are not hydrated in the condition, Table S1, Supporting Information. The more negative hydration enthalpy attained for 60Sc indicates a higher proton concentration at the intermediate temperatures.

The total proton conductivity, reflecting both the bulk and grain boundary resistivities in the polycrystalline pellet, exceeds 0.01 S cm⁻¹ at 60-at% Sc doping between 396 and 534 °C under a water partial pressure, pH₂O, of 0.02 atm, Figure 1a. The temperature to attain 0.01 S cm⁻¹ is 54 °C lower than for 20-at% Y-doped barium zirconate (20Y).[7] Compared with 20Sc, the total conductivity in HSBZ was enhanced by a factor of eight below 390 °C. In contrast to the Y-doped system, the proton conductivity increases with increasing Sc content at 400 °C, which led to the required total conductivity of 0.01 S cm⁻¹ in the 60-at% Sc at 396 °C, Figure 1b.

An isotope exchange experiment between D₂O and H₂O moisture revealed that the proton is the main carrier for the ionic conduction in 60-at% Sc-doped barium zirconate. A sudden change from D₂O to H₂O moisture while maintaining the partial pressure replaces deuterons with protons in the pellet. When the proton is the main carrier, an isotope effect with a factor of 1.41, (m₃/m₁)¹/², would be obtained because...
of the change in the vibrational frequency proportional to the square root of the mass, \( m_i \), of carrier species \( i \).\[20\] To perform such an experiment, a 60Sc pellet was equilibrated for a long time at 400 °C under \( p_{\text{D}2\text{O}} = 0.02 \) atm, where the obtained conductivity was 0.078 S cm\(^{-1}\), Figure 1c. When the atmosphere was changed to water vapor at the same partial pressure, the conductivity gradually increased to 0.013 S cm\(^{-1}\) with an enhancement of 1.7, which is close to the theoretical value of the isotope effect. This result strongly supports that the proton is the main carrier for the conduction at intermediate temperatures. A fast proton conduction of 0.013 S cm\(^{-1}\) was repeatedly attained at 400 °C during the isotope exchange experiment of 200 h. The pellet showed sufficient chemical stability during proton insertion and extraction at the target temperature.

AC impedance analyses in Figures S3–S7 (Supporting Information) show that the bulk proton conductivity in 60Sc is ten times higher than that of 20Sc around 270 °C, Figure 1d. Compared with 20Sc, the apparent activation energy for proton conduction was reduced by 6 kJ mol\(^{-1}\), whereas the pre-exponential factor was enlarged by a factor of two, Table 1 and Figure S7b, Supporting Information. A clear contribution from the grain boundaries in the 60Sc sample was found only near room temperature, Figure S3 (Supporting Information), suggesting a small resistivity across the grain boundaries. The effective grain boundary conduction of 60Sc is 17 times higher than that of 20Sc, although the activation energies were almost equivalent to each other with values of 64 kJ mol\(^{-1}\). The activation energy was also equivalent to that reported for a Y dopant,\[7\] Table 1 and Figure S7c, Supporting Information. Additional DC measurement in Figure S6 (Supporting Information) confirmed the assignments of bulk and grain boundary contributions assigned by the impedance analyses. Heavy Sc-doping enhanced both the bulk and grain boundary conductivities, which led to a high total conductivity at intermediate temperatures.

The bulk proton diffusivities, determined from the Nernst–Einstein relationship using the measured proton concentration and bulk proton conductivities, showed an enhancement by a factor of 2.5 below 390 °C, Figure 1e. The apparent activation energies for the proton diffusion determined for 20Sc and 60Sc below 200 °C were 49.0 ± 0.2 and 41.4 ± 0.5 kJ mol\(^{-1}\), respectively, with 60Sc showing an ~8 kJ mol\(^{-1}\) smaller value. Within the same host oxide, the apparent activation energy, especially at the low temperatures, reflects the degree of proton trapping.\[12\] The smaller activation energy in 60Sc thus suggests a reduced trapping energy. This reduced trapping energy combined with the higher proton concentration resulted in a 2.5-times enhancement in the bulk proton conductivity of the 60Sc sample.

An additional AC impedance experiment under a high water partial pressure of 2.4 atm further confirmed the above assignments. The hydration thermodynamics reveals that the high water partial pressure increases the proton concentration at high temperatures.\[19\] Under \( p_{\text{H}_{2}\text{O}} = 2.4 \) atm, a proton concentration of 0.55 mol per formula unit in the 60Sc sample would be maintained up to 600 °C, Figure S8a, Supporting Information. The high water partial pressure should thus lead to an enhanced bulk proton conductivity because of the increase in proton concentration above 300 °C while maintaining the bulk proton diffusivity for the entire temperature range. Our experiment exactly demonstrated that, as shown in Figure 1a and Figure S8b, Supporting Information.

The heavy Sc doping enhanced the grain growth by a surprising amount, as well as the specific grain boundary conductivity of polycrystalline samples. In the 60Sc pellet, the grain size ranged from 0.5 to 20 \( \mu \)m, with a representative diameter of 6.7 ± 0.2 \( \mu \)m and a standard deviation of 4.8 ± 0.3 \( \mu \)m, Figure 2a,b. This is almost seven times larger than those of 20Sc and 20Y,\[7\] Figure S9b, Supporting Information. The grain growth reduced the density of the resistive grain boundary across the 60Sc pellet. The heavy Sc doping enhanced the specific grain boundary conductivity by 20-fold, Figure 2c. The specific grain boundary conductivity in 60Sc is ten times higher than that in 20Y.\[7\] Although it is not known why the specific grain boundary resistance was reduced, the heavy Sc doping made the contribution of the resistive grain boundaries to the total almost negligible at the intermediate temperatures.

To investigate the chemical stability of the 60Sc sample against \( \text{CO}_2 \), we performed an accelerated stability test under a concentrated and humidified \( \text{CO}_2 \) stream at 400 °C by in situ X-ray diffraction. Barium zirconate is thermodynamically favored to form BaCO\(_3\) below ~500 °C under 1 atm of carbon dioxide.\[21\] To accelerate the extent of possible decomposition, the extreme condition, flowing \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) mixed gases with respective partial pressures of 0.98 and 0.02 atm against the powder sample, was chosen. The 60Sc sample was first hydrated in the X-ray chamber at 400 °C for 5 h under humidified nitrogen with a water partial pressure of 0.02 atm. A very small hump over the background exists at around 23.7°, the main peak position of the BaCO\(_3\) phase shown as a blue arrow in Figure 3a and Figure S10, Supporting Information. The estimated amount was 0.46 wt%. This is probably caused by a slight deviation in the chemical composition from the barium stoichiometry, as evidenced by the ICP-OES. As a reference at hand, the atmosphere was changed to the highly concentrated \( \text{CO}_2 \) stream while maintaining the water partial pressure. The intensity of the BaCO\(_3\) phase was almost unchanged for 240 h during the accelerated test, Figure 3a and Figure S10, Supporting Information. The possible increase in the BaCO\(_3\) phase
estimated from the ratio in the strongest peak intensities of BaCO3 and perovskite was 0.1 wt%, Figure 3b. Accordingly, almost no shift was observed for the main peak assigned to the perovskite, where the estimated change in the lattice constant was 0.02%, Figure 3c. Considering there was 2450 times more CO2 content in the test condition over the ambient atmosphere, 400 ppm, the accelerated stability test is equivalent to 67 years of exposure to the ambient atmosphere at 400 °C. Although it is not clear that the result reflects the thermodynamics and/or kinetics, the 60-at% Sc-doped barium zirconate showed sufficient stability against the CO2-containing atmosphere at 400 °C.

In summary, we developed a stable proton-conducting poly-crystalline oxide that exhibits a high total proton conductivity of 0.01 S cm−1 in the temperature range between 396 and 534 °C under a water partial pressure of 0.02 atm. The key to achieving the high total conductivity and chemical stability was the heavy doping of Sc into barium zirconate. It simultaneously enhanced the proton concentration, proton diffusivity, specific grain boundary conductivity, and grain growth, which overcame the trade-off relationship between fast ionic conduction and chemical stability in conventional materials. Although the development of electrochemical devices has yet to be explored, this study proposes a promising candidate for the electrolyte of solid-state electrochemical devices operated at intermediate temperatures.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.
Keywords

grain growth, heavily proton- and Sc-doped barium zirconate (HSBZ), high tolerance against CO₂, high total proton conductivity, proton trapping, proton-conducting oxides

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