

BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} 质子导体的电化学性能

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摘 要: Y 掺杂的 BaZrO₃ 因其优异的化学稳定性而被广泛研究。然而, 较高的烧结温度限制了其应用。为改善 BaZrO₃ 的烧结活性, 对 Y-BaZrO₃ 采用 Pr³⁺ 和 Ni²⁺ 进行共掺杂, 并对其微观形貌及电化学性能进行研究。Ni 与材料形成固溶体, Pr³⁺ 的掺杂增大了晶粒尺寸, 这对致密化过程极为重要。XPS、Raman 和 EPR 结果表明, 少量 Pr³⁺ 掺杂可以增加材料的氧空位含量, 并通过加速水的解离和吸附促进质子进入, 从而促进质子传导。然而, 过量 Pr³⁺ 掺杂导致的高浓度氧空位会产生缺陷缔合反应, 使低温下的电导率略有下降。随着温度的升高, 氢分离膜的氢渗透性也增加。此外, BaZr_{0.66}Y_{0.2}Pr_{0.1}Ni_{0.04}O_{3-δ} 的氢渗透性高于 BaZr_{0.71}Y_{0.2}Pr_{0.05}Ni_{0.04}O_{3-δ}, 在 1 173 K 时, 氢渗透性达到 $2.60 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ 。

关键词: 氧空位; 质子电导率; 氢分离膜

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Electrochemical Properties of BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} Proton Conductors

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Abstract: Y-doped BaZrO₃ proton conductor has been extensively studied due to its outstanding chemical stability. However, the high sintering temperature has limited its practical application. To enhance the sintering activity of BaZrO₃, we co-doped Y-BaZrO₃ with Pr³⁺ and Ni²⁺, and investigated its microscopic morphology and electrochemical properties. The introduction of Ni forms a solid solution with the sample, while Pr³⁺ doping increases the grain size, a critical factor for the densification process. XPS, Raman and EPR results reveal that a small amount of Pr³⁺ doping significantly raises the concentration of oxygen vacancies in the materials. This increase promotes proton incorporation by accelerating the dissociation and adsorption of water, thereby facilitating the proton conduction. However, it's important to note that excessive Pr³⁺ doping leads to a high concentration of oxygen vacancies, which triggers a defect association reaction. Consequently, this results in a slight decrease in conductivity at low temperatures. On the other hand, as the temperature increases, the hydrogen permeability of the membrane increases also rises. Moreover, the hydrogen permeability of BaZr_{0.66}Y_{0.2}Pr_{0.1}Ni_{0.04}O_{3-δ} is found to be higher than that of BaZr_{0.71}Y_{0.2}Pr_{0.05}Ni_{0.04}O_{3-δ}, with the former reaching $2.60 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ at 1 173 K. Notably, these membranes exhibit remarkable in CO₂-containing atmosphere indicating excellent resistance to CO₂.

Keywords: oxygen vacancy; proton conductivity; hydrogen separation membrane

1 Introduction

With the exacerbation of the global energy crisis and the increasingly escalating air pollution, hydrogen is gaining increased attention as a sustainable and

clean energy source^[1]. Currently, hydrogen is predominantly produced through coal gasification, reforming, partial oxidation of natural gas, or water gas shift reactions, which often yield various byproducts simultaneously^[2]. Consequently, the separation and

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purification of hydrogen from other gases to obtain pure hydrogen have become crucial aspects of hydrogen production. Hydrogen purification technologies mainly include pressure swing adsorption, and membrane separation. Membrane separation method involves various types of membranes, such as dense metal membranes, inorganic porous membrane, metal–organic framework membrane, organic polymer membrane and mixed proton electron membrane^[3–4]. Among these, dense ceramic mixed proton electron conducting membranes theoretically have 100% hydrogen selectivity, as hydrogen is separated in the form of protons rather than molecules^[5]. One advantage of this approach is that it does not require electrodes or external circuits. Instead, the driving force for hydrogen transport is provided by the hydrogen chemical potential gradient^[6]. As a result, hydrogen separation membranes based on dense, mixed electron and proton conduction are considered to be more cost-effective than traditional gas separation technologies.

These membranes hold great promise in efficiently purifying hydrogen, addressing the pressing global energy and environmental challenges we currently face.

Mixed conductor hydrogen separation membranes rely heavily on the performance of proton conductors, which play a crucial role in their functionality. Perovskite oxides (ABO_3) have garnered extensive attention as unique metal oxides due to their exceptional stability, tunable structure, and good proton conductivity^[7]. Presently, the most advanced proton conductor ceramics encompass two types: cerate and zirconate-based oxides, as well as their solid solutions. Among these, BaCeO_3 -based proton conductors exhibit superior proton conductivity. For instance, $\text{BaCe}_{0.7}\text{Y}_{0.3}\text{O}_{3-\delta}$ demonstrates a high conductivity of $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 873 K ^[8]. However, their practical application is hindered by the instability of BaCeO_3 in CO_2 and H_2O -containing atmospheres^[9–11]. In contrast, Y-doped BaZrO_3 exhibits better chemical stability owing to the higher electronegativity of Zr ions, but its total conductivity remains relatively low^[12]. Unfortunately, BaZrO_3 suffers from unsatisfactory sintering activity, necessitating prolonged sintering at high temperatures to achieve densification of the bulk material^[13]. Such elevated sintering temperature can lead to Ba volatilization and alteration in the material components, resulting in reduced electrical conductivity^[14]. Therefore, finding an effective method to enhance both the sintering activity and conductivity of BaZrO_3 is imperative. Numerous efforts have been made to enhance the sintering capability of BaZrO_3 , with the most common approach involving the use of sintering additives. Various additives like NiO ^[15], CuO ^[16], ZnO ^[17], CaO ^[18] and LiNO_3 ^[19] have been successfully employed to

improve the sintering ability of BaZrO_3 and reduce the sintering temperature. However, the use of such additives may introduce undesirable electronic conduction in the electrolyte^[17] leading to a decrease in the total conductivity^[20]. Another method to improve the sinterability of BaZrO_3 is the substitution of Zr^{4+} with trivalent or tetravalent metal cations^[21]. Trivalent metal cation doping not only promote the sinterability, but also increase the presence of oxygen vacancies, consequently enhancing proton conductivity^[22–24]. The introduction of dopants causes to changes in defect concentration and transition metal oxidation states, leading to different lattice distortions and the appearance of oxygen defects. Moreover, variations in dopant particle size and charge can increase the oxygen diffusion coefficient and the surface exchange coefficient, contributing to the activation energy and the proton conductor activity. More oxygen vacancies can be successfully induced in the material lattice by doping with +3 valence rare earth ions including Y^{3+} , Yb^{3+} , Sm^{3+} , Gd^{3+} and Pr^{3+} at the B-site^[25–27]. Y^{3+} has been focused as one of the most representative non-equivalent dopants^[21], a key challenge in the development of proton conductor materials is to simultaneously achieve easy hydrogen binding and low energy barriers for proton migration^[28–32]. However, despite Y-doped BaZrO_3 showing promise, achieving a dense microstructure still requires a high sintering temperature and a prolonged sintering time. To address this issue, some rare earth ions, such as Pr and Nd, have been explored as dopants to alter the sintering behavior of the substrate material^[33]. Studies have shown that Pr doping improves the sintering performance of ceramic electrolytes, decreases the sintering temperature, and densifies the proton conducting material^[34]. Co-doping with Y and Pr in BaZrO_3 increases its conductivity in wet atmospheres, and the activation energy decreases from about 0.55 eV to 0.40 eV with higher Pr^{3+} content^[35]. Additionally, Ni-doped $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ exhibited adequate proton conductivity and excellent sinterability^[21]. Therefore, the co-doping of Ni^{2+} and Pr^{3+} may not only enhance sintering activity but also lead to higher proton conductivity, improving the selectivity and hydrogen permeation activity.

In this study, the focus is on developing ceramic membrane materials with sufficient protonic conductivity and considerable stability for hydrogen separation at high temperatures. The Pr^{3+} and Ni^{2+} co-doped proton conductor $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ perovskite was prepared, and the phase structure, microstructure, conductivity and stability were thoroughly investigated. Additionally, the influence of dopant ions on surface defect formation and the hydrogen permeability was studied in detail.

2 Experimental section

BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} ($x=0, 0.05, 0.10$) powders were synthesized via the sol-gel synthesis route. Firstly, Y₂O₃ was dissolved into a solution of nitric acid diluted with deionized water. Then the stoichiometric amounts of Ba(NO₃)₂, Zr(NO₃)₄·5H₂O, Ni(NO₃)₂·6H₂O and Pr(NO₃)₃·6H₂O were added while stirring. Once the raw materials were completely dissolved and a clear ionic solution was formed, citric acid was added as the complexing agent with a molar ratio of 1.0:1.5 to metal ions and the pH of the solution was adjusted to approximately 7 using ammonia during the complexation process. Subsequently, the solution was continuously stirred at 353 K until it formed a viscous gel, which was then heated and spontaneously ignited to obtain the precursor powder. Finally, the as-prepared powders were calcined at 1 373 K in air for 6 h to form pure perovskite phase samples. After sufficient grinding, the BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} pellets were prepared using a uniaxial pressing method with a pressure of 4 MPa. The circular pellets were then sintered at 1 823 K for 10 h in air to obtain the dense ceramic samples.

The phase structure of the sintered powders and ceramic membrane samples was analyzed using X-ray diffractometer (Bruker D8 Advance, Germany, XRD). Moreover, the bond energy changes of the powders were characterized by Raman spectroscopy combined with X-ray photoelectron spectroscopy (Thermo Scientific ESCALAB 250Xi, America, XPS). Meanwhile, the oxygen vacancy concentration changes of the doped samples were analyzed by electron paramagnetic resonance (Bruker EMXplus, EPR). The surface and cross-sectional morphology of the ceramic membrane samples were observed using scanning electron microscopy (ZEISS Sigma 300, Germany, SEM).

The silver paste was coated on both sides of the pellet and calcined at 973 K for 1 h. The total resistance of the BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} membrane was determined by electrochemical impedance spectroscopy, performed using an electrochemical workstation (Shanghai Chenhua, CHI660E) in the temperature range of 773–1 073 K. The bias voltage was 10 mV and the sweeping frequency was 1.0 MHz–0.1 Hz. The tests were conducted in an atmosphere of wet hydrogen (3% H₂O), air and nitrogen, with a gas flow rate of approximately 30 mL·min⁻¹. The activation energy was calculated using the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E}{k_B T}\right) \quad (1)$$

where σ is conductivity; σ_0 is preexponential factor; E is activation energy; k_B is Boltzmann constant, 8.617 330 3×10⁻⁵ eV/K; and T is the thermodynamic temperature.

The dense BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} membranes were polished with 180, 600, and 2 000 mesh sandpapers, respectively, until the thickness reached 0.4 mm. Then, Pt paste was painted on the entire surface and calcined at 973 K for 1 h. The membrane was sealed to an Al₂O₃ tube with a glass ring at 1 353 K for 60 min. One side of the membrane was exposed to H₂/N₂ mixed gas which had been completely mixed using a gas mixer, while the other side was flushed with Ar as the sweeping gas at a flow rate of 20 mL·min⁻¹. The composition of the gas on the sweep side was analyzed using a gas chromatograph (Fuli, GC-9790).

3 Results and discussion

To investigate the impact of cationic doping amounts on the phase structure, the X-ray diffraction patterns were conducted for BaZrO₃ (BZ), BaZr_{0.8}Y_{0.2}O_{3-δ} (BZY), BaZr_{0.76}Y_{0.2}Ni_{0.04}O_{3-δ} (BZYN4), BaZr_{0.71}Y_{0.2}Pr_{0.05}Ni_{0.04}O_{3-δ} (BZYP5N4) and BaZr_{0.66}Y_{0.2}Pr_{0.1}Ni_{0.04}O_{3-δ} (BZYP10N4) powders, all calcined at 1 373 K for 6 h in air, as depicted in Fig. 1(a). Pr³⁺ and Ni²⁺ co-doped BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} powders exhibit a cubic perovskite phase, as depicted with the standard PDF card (06–0399) and no impurity diffraction peak is observed in any of the samples^[36]. Notably, the peaks of BZY, BZYN4, BZYP5N4 and BZYP10N4 samples in the 110 lattice plane are shifted to a lower angle compared with BZ. This phenomenon is attributed to the larger ionic radius of Y³⁺ and Pr³⁺ ions compared to Zr⁴⁺, thus successful doping leads to lattice expansion^[34]. The lattice parameters calculated from XRD data are presented in Table 1. The introduction of Pr³⁺ and Ni²⁺ into the BZY lattice results in an increase in the cell volume, further confirming the successful incorporation of Pr³⁺ and Ni²⁺ into the perovskite lattice^[5, 37].

Table 1 Cell parameters and volumes

Sample	$a/\text{\AA}$	$V/\text{\AA}^3$
BZ	4.192 87	73.71
BZY	4.207 42	74.48
BZYN4	4.213 78	74.82
BZYP5N4	4.226 44	75.50
BZYP10N4	4.229 96	75.68

Doping generally alters the energy required for oxygen vacancy (V_O) generation and the oxygen diffusion potential in the lattice of the chalcogenide^[35]. To investigate the impact of doping on the oxidation state modification and to characterize the change in oxygen vacancy, BZYN4, BZYP5N4 and BZYP10N4 membranes were analyzed using XPS. The obtained spectra were charge corrected with reference to the binding energy of C 1s (284.8 eV). The high-resolution XPS spectra of O 1s for BZYN4, BZYP5N4 and BZYP10N4 are shown in Figs. 1(b)–1(d), respectively.

The O 1s peak consists of three components, lattice oxygen (O_{lat}), chemisorbed oxygen (O_{ads} : O_2^{2-}/O^- , OH^-/CO_3^{2-}) and oxygen in the hydroxyl environment (O_{H})^[38]. Notably, that the proportion between O_2^{2-}/O^- and O_{lat} indicates the oxygen vacancy content^[38–41]. The $(O_2^{2-}/O^-)/O_{\text{lat}}$ ratio is 0.37 for BZYN4, 0.55 for BZYP5N4, and 0.83 for BZYP10N4, indicating an increase in oxygen vacancy content increases with a small amount of Pr^{3+} doping. Furthermore, the binding energy of O_{lat} is 529.21 eV for BZYN4, while it

decreases to 529.07 eV for BZYP5N4, and 528.83 eV for BZYP10N4. These differences indicate changes in electron density around the doped cations, likely caused by electron transfer around the doped metal cations. The electron density around the oxygen ion increases with the concentration of doped Pr^{3+} ions, implying that the O atom in BZYP10N4 is more active but potentially detrimental to chemical stability^[42]. In conclusion, the XPS spectra suggest that a small amount of Pr^{3+} doping

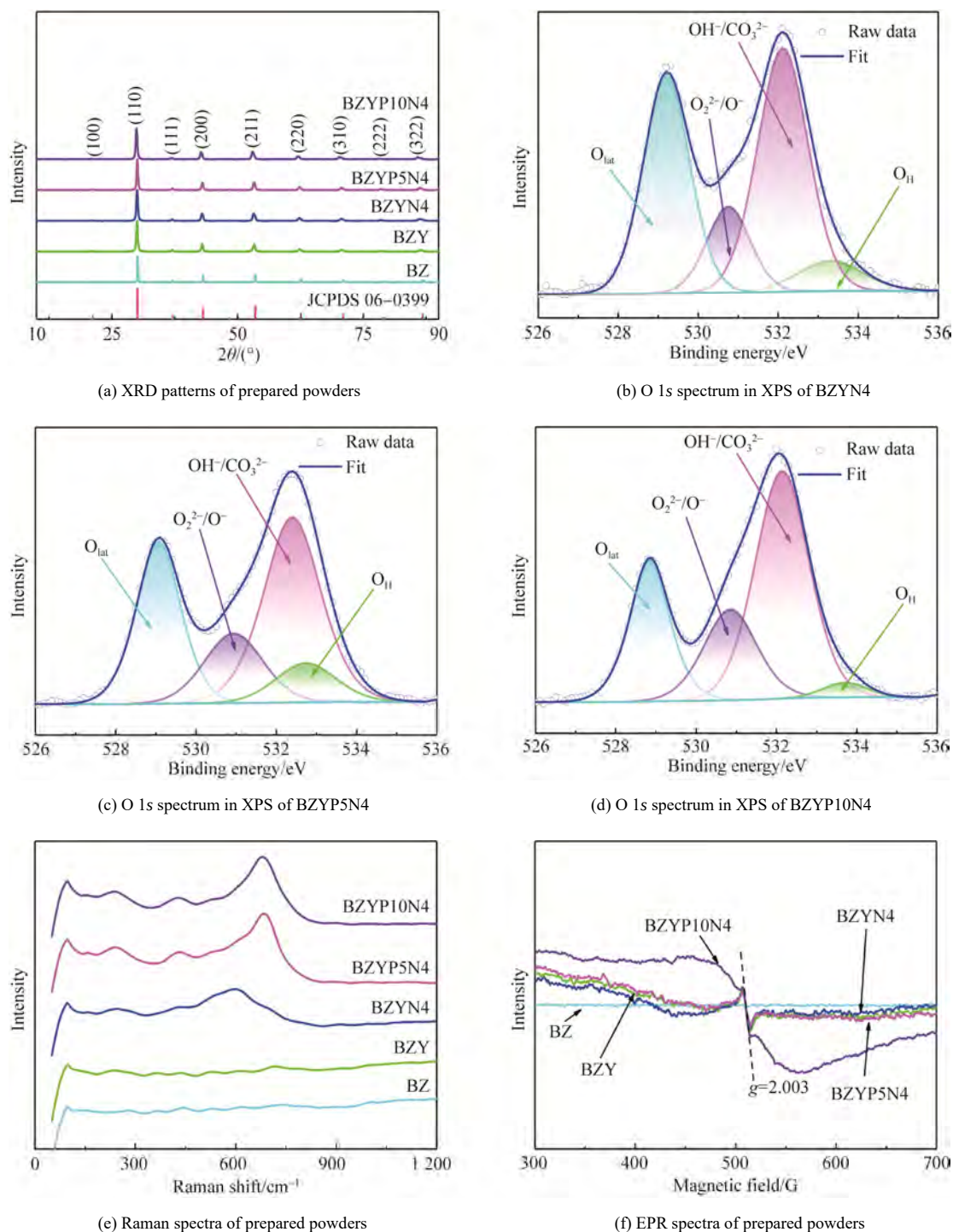


Fig. 1 Characterization of prepared powders

can enhance the oxygen vacancy concentration of BaZrO_3 . This enhancement can facilitate the incorporation of protons by accelerating the dissociative adsorption of water^[22, 43], potentially benefiting proton conductivity.

Furthermore, metal cation doping can not only affects the concentration of oxygen vacancies in the samples, but also influences the proton diffusion mechanism by altering the binding bonds, such as proton positions, proton migration paths, and energy potentials^[22], etc. The diffusion paths can be categorized into bulk diffusion, surface diffusion and grain boundary diffusion. When a proton moves from one equilibrium position to another adjacent equilibrium position in a crystal structure, it must overcome a free energy barrier, which represents the resistance to proton diffusion. In undoped materials, the protons primarily diffuse on the surface due to the scarcity of oxygen vacancies and the high energy barrier. However, the doping of low-valent metal cations increases the concentration of oxygen vacancies by changing the charge, enabling the proton to diffuse through the oxygen vacancy for bulk diffusion^[8]. This increase in oxygen vacancy concentration reduces the energy barrier, making proton conduction more favorable. To investigate the effect of doping on local structural changes, Raman spectra were applied to the sintered powders, as shown in Fig. 1(e). Typically, ideal cubic perovskite oxides do not exhibit any Raman signal^[44]. However, the lattice disorder caused by the disturbance of cubic symmetry or the formation of oxygen vacancies due to doping leads to the generation of Raman signal^[45]. The Raman scattering observed around 98 cm^{-1} and 200 cm^{-1} arise from the deformational motion and stretching vibrations of $\text{Ba}-[\text{Zr/Y}]-\text{O}_6$ unit^[46]. The vibrational modes around 428 cm^{-1} correspond to the asymmetric stretching of $\text{O}-\text{Zr}-\text{O}$ in the opposite directions. Remarkably, the intensity of vibrational modes on 428 cm^{-1} is found to

be stronger in BZYP5N4 and BZYP10N4, possibly due to the presence of secondary phase stretching vibration from $[\text{Zr/Y}]-\text{O}_2$ ^[47]. Additionally, with the increase of Pr^{3+} concentration, the intensification of the 428 cm^{-1} band may be attributed to the formation of oxygen vacancies^[46]. Furthermore, the wavelength region around $600-800\text{ cm}^{-1}$ corresponds to $\text{Ba}-\text{O}$ stretching and bending modes^[48]. The observed changes in the vibration band and intensity of the doped samples compared to undoped barium zirconate are due to the introduction of larger ion radius Pr^{3+} and the generation of oxygen vacancies.

Both XPS and Raman spectroscopy confirm that metal ion doping leads to the generation of oxygen vacancies. To further investigate the variation of oxygen vacancy concentration, the powder samples were characterized by electron paramagnetic resonance (EPR) analysis and the result was shown in Fig. 1(f). Since BaZrO_3 is a non-magnetic (no unpaired electron in Ba^{2+} , Zr^{4+} or O^{2-}), it does not have its own EPR signal^[49]. The signal observed in the doped BaZrO_3 located at $g=2.003$ can be attributed to oxygen vacancies^[50], which not only confirms the existence of oxygen vacancy more intuitively but also aligns with the analysis results of XPS and Raman spectroscopy. Additionally, the intensity of the EPR peaks further confirm that the oxygen vacancy concentration increases with Pr^{3+} concentration.

The influence of doping ions on the microstructure was systematically characterized using scanning electron microscopy (SEM). The cross-sectional and surface morphology of the BZY, BZYN4, BZYP5N4 and BZYP10N4 membranes sintered at 1823 K for 10 h are shown in Fig. 2. Many pores are visible in BZY, which is typical for ceramics that require high temperature and prolonged sintering to achieve dense compaction. However, the high sintering temperature can easily lead to volatilization of metal cations and cause changes in the material components, ultimately

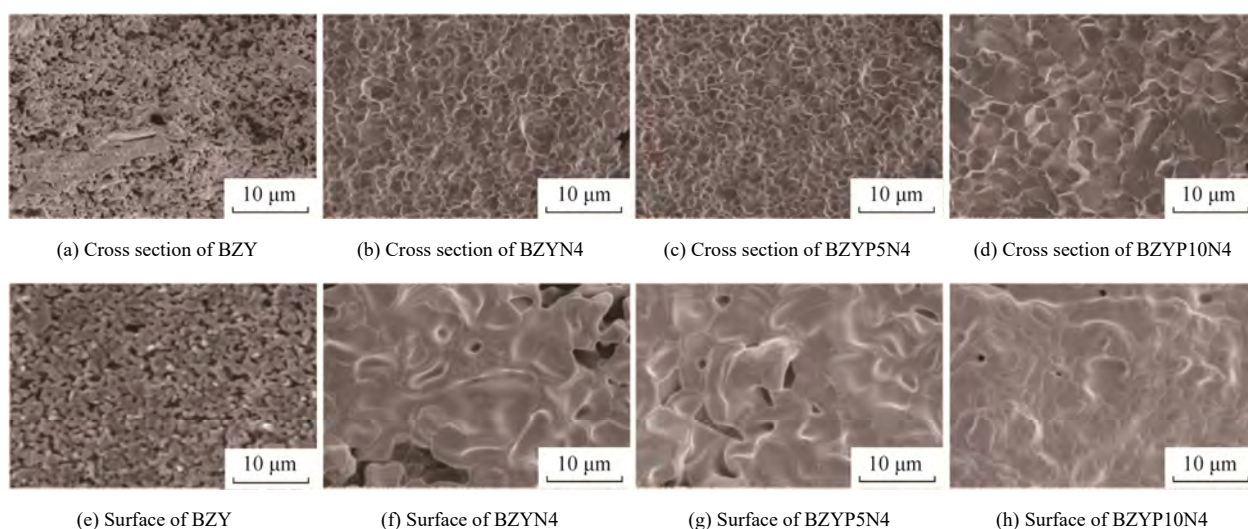


Fig. 2 SEM images of sintered samples at 1823 K for 10 h

reducing the conductivity^[14]. In contrast, clear observations reveal large-sized grains and very few pores in BZYN4, BZYP5N4 and BZYP10N4. Notably, the grain size of the sample becomes significantly larger after Ni²⁺ doping, and it further increases with the addition of 10% (in mole) Pr³⁺ doping. The apparent density of the samples was measured using the Archimedes method with water as soaking medium. The theoretical density was calculated based on lattice parameters. And the relative density of the sample was obtained from the ratio of the apparent density to the theoretical density. The relative density of BZY is only 85.3%, whereas BZYN4, BZYP5N4 and BZYP10N4 exhibit higher relative densities of 91.3%, 92.2% and 94.1%, respectively. The increase in relative density indicates that the Pr³⁺ and Ni²⁺ doping contributes to the improved sintering of the samples, consistent with the SEM results. Ni can reduce the sintering temperature by forming a solid solution with the sample, distorting the lattice of perovskite structure^[51], and facilitating activation and lower

sintering temperature.

When Pr³⁺ ($r=0.99 \text{ \AA}$) replaces Zr⁴⁺ ($r=0.72 \text{ \AA}$), the metal cation doping creates oxygen vacancies that promote the diffusion of oxygen ions in the oxide lattice, which is extremely important for the densification process^[52]. Moreover, the metal ion with larger radius increases the volume of the free lattice and the mobility of cations, particularly at grain boundaries, promoting the growth of grains^[53]. The lower grain boundary density in the sintered samples theoretically contributes to better conductivity^[54].

Furthermore, EDS spectra in Fig. 3 confirm that each element is uniformly distributed in the BZYP5N4 and BZYP10N4 samples, with no obvious element segregation. This reflects the successful incorporation of Pr³⁺ and Ni²⁺ into the BaZrO₃ lattice, facilitating the uniform distribution of oxygen vacancies and good connectivity between the respective grains. These factors are beneficial for ensuring smooth electron and proton transport within the bulk phase of the membrane.

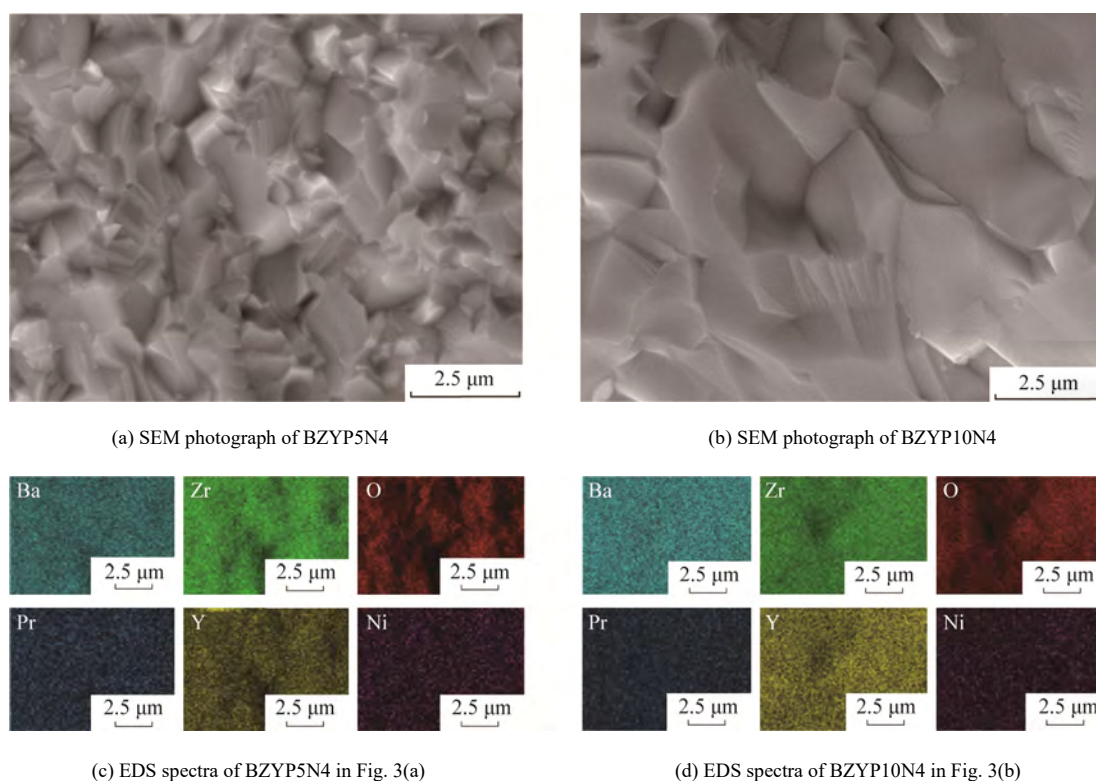
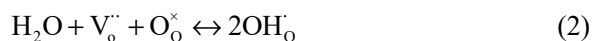


Fig. 3 Elemental distribution images

In a humid environment, oxygen vacancies on the surface of proton conducting perovskite oxides become the active sites for the dissociation of water from the gas phase into hydroxide ions and protons. The process can be described as follows^[55]:



The hydroxide ions fill the oxygen vacancy sites, and the protons are transported from one lattice

oxygen site to another by attaching to the lattice oxygen through covalent bonds. The hydroxyl ion can be viewed as an interstitial proton attached to the lattice oxygen. The small size of the proton allows it to be transported by attaching to the lattice oxygen ion of the active species. The relationship between electron conductivity and oxygen vacancy can be explained by the equilibrium relationship between oxygen vacancy and oxygen partial pressure^[56]:



When electron-hole pairs are present, the effect of water vapor on the conductivity in humid atmosphere can be explained by equations (2) and (3). The entry of water vapor into the surface of the material leads to the depletion of oxygen vacancies (equation (2)). This depletion is accompanied by a shift of the equilibrium of equation (3) from the generator side to the reactant side^[57]. Therefore, the oxygen vacancy and atmosphere play a crucial role in the electrical conductivity of the samples.

Fig. 4 shows the total electrical conductivities of $\text{BaZr}_{0.76-x}\text{Y}_{0.2}\text{Pr}_x\text{Ni}_{0.04}\text{O}_{3-\delta}$ under different atmospheres. As SEM images show that there are many pores inside BZY, it is meaningless to test its conductivity. On the one hand, the introduction of Pr^{3+} will promote grain growth and then reduce the grain boundary resistance. The conductivity of BZYP10N4 is superior to that of BZYP5N4 in humid atmosphere of 20% H_2 +80% N_2 at high temperature, which can be explained by the Vehicle mechanism^[58]. In humid atmosphere of 20% H_2 +80% N_2 , the conductivity is dominated by proton conductivity. Water vapor provides a new pathway for proton incorporation, which increases the concentration

and mobility of protons in oxides^[59], resulting in higher proton conductivity. On the other hand, the high concentration of oxygen vacancies caused by Pr^{3+} doping can lead to defect association reactions. At the low temperature, defective conjugation caused by excessive oxygen vacancies in BZYP10N4 is the key factor leading to a slight decrease in conductivity^[60-61]. There is a slight decrease in conductivity after Pr^{3+} doping, which may be due to the lattice distortion caused by the larger radius of Pr^{3+} ions. The activation energy, calculated by equation (4), in wet air (0.63, 0.65 eV and 0.84 eV for BZYN4, BZYP5N4 and BZYP10N4, respectively) was larger than that of the energy value c calculated in wet H_2 (0.23, 0.26 eV and 0.51 eV for BZYN4, BZYP5N4 and BZYP10N4, respectively), indicating that in humid H_2 environments, proton conductivity dominates, while in wet air, mixed oxygen ions and electron conductivity coexist^[34, 62]. It is noteworthy that the activation energy of BZYP10N4 is larger than that of BZYP5N4 in H_2 and air, which may be caused by excessive lattice distortion due to the substitution of more Pr^{3+} .

A diagram of the hydrogen permeation process is presented in Fig. 5. The feed gas contains 20% H_2 and

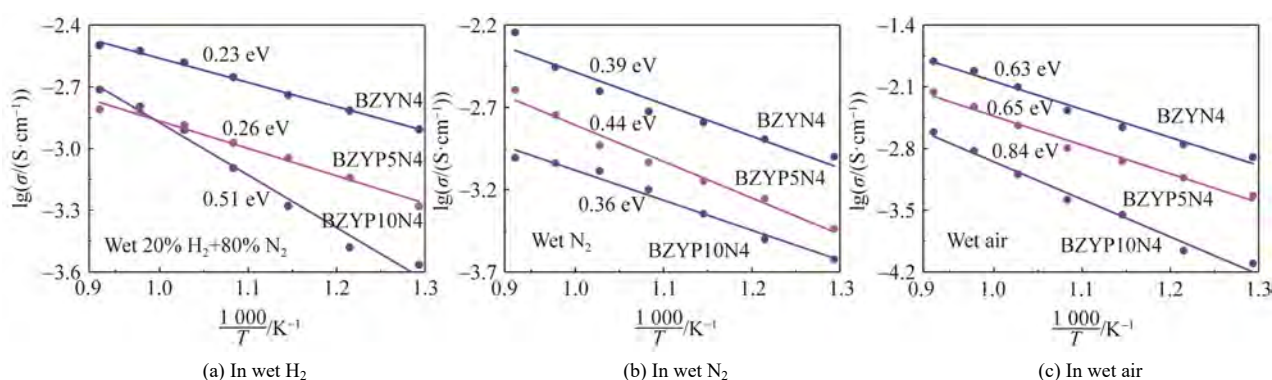


Fig. 4 Conductivity curves of samples

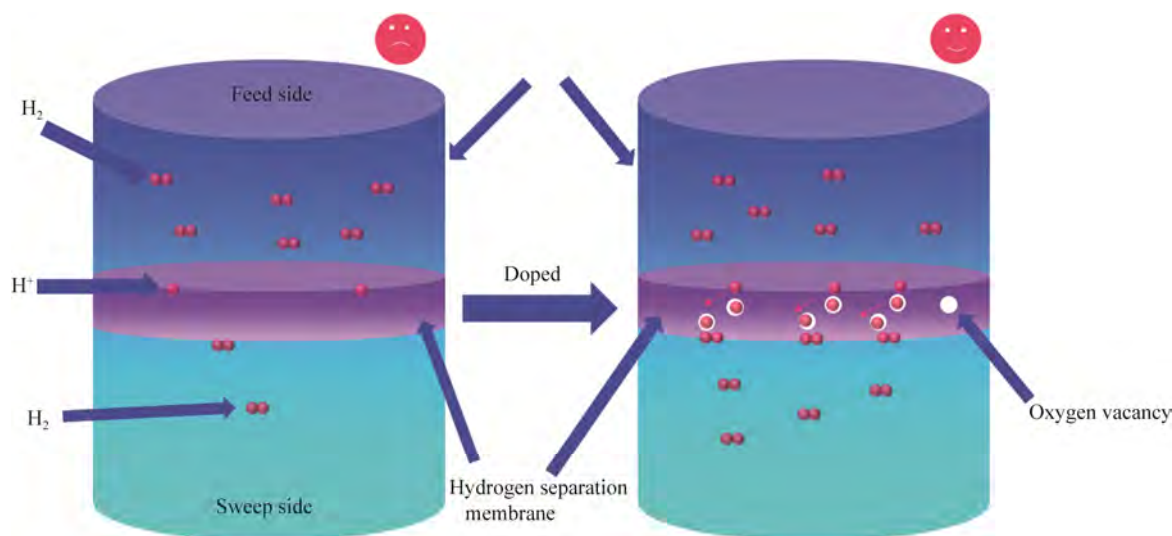


Fig. 5 Schematic of hydrogen permeation

80% N₂, while high-purity Ar is used as the sweep gas. As a result, there exists a difference of hydrogen chemical potential gradient on both sides of the membrane, causing hydrogen diffuse from the high chemical potential side to the low chemical potential one. On the side of feed gas, H₂ is catalyzed by Pt on the membrane surface, leading to the dissociation of H₂ into H⁺ ions and electrons (e⁻). The H⁺ ions then move through the bulk of the membrane, while the electrons migrate to the other side through the surface of the membrane. On the side of sweep gas, H⁺ and e⁻ recombine to form hydrogen, effectively achieving the purpose of hydrogen separation. The proton transport in the chalcogenide material follows the Vehicle mechanism, which relies on hydroxyl conduction. Oxygen ions within the hydroxyl groups act as the transporters in the transport process. Oxygen ion diffusion is influenced by the concentration of oxygen vacancies, which are introduced by doping metal cations. As a result, the rate of proton transport is

affected by the rate of oxygen ion diffusion, and the oxygen vacancies created by metal cation doping facilitate the transport of protons within the ceramic membrane bulk phase.

Both the proton migration in ceramic hydrogen separation membranes and the embedding of water on the sample surface into the proton conductor are thermally activated processes. Therefore, the temperature during the reaction can have a significant impact on the hydrogen permeation performance. The temperature dependence of hydrogen permeation flux (J_{H_2}) of the BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} membrane is shown in Fig. 6(a). The J_{H_2} increases with the temperature from 1 023 K to 1 223 K, indicating that hydrogen transport of the BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} membrane is a thermally activated process. The J_{H_2} of BZYN4, BZYP10N4 and BZYP5N4 are $3.46 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, $2.60 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ and $1.75 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, respectively, at 1 173 K.

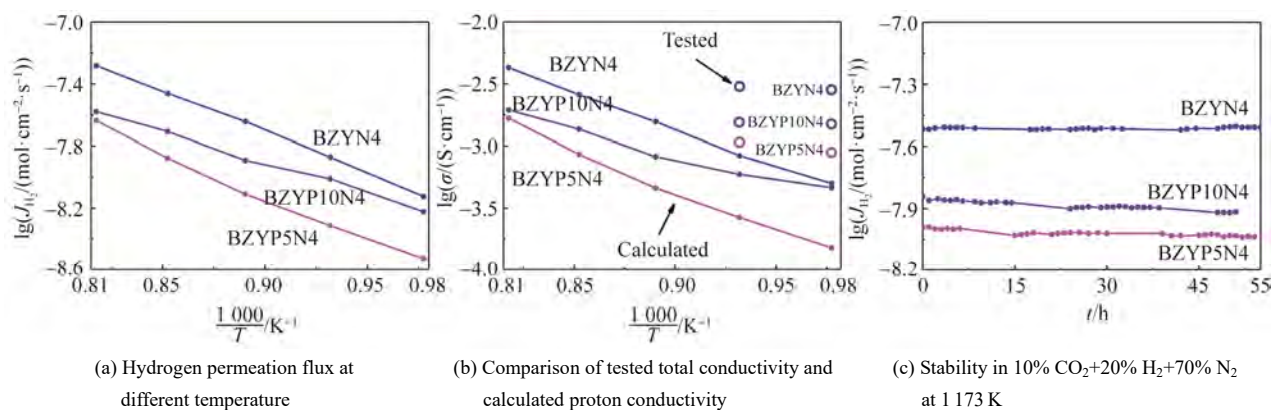


Fig. 6 Hydrogen permeation test curves of BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ}

The hydrogen permeability obtained in this study is compared with some metal ceramic membranes from the literature, as listed in Table 2. As seen from Table 1, the hydrogen permeation fluxes of Ni-Ba(Zr_{0.7}Pr_{0.1}Y_{0.2})O_{3-δ} cermet membranes in 3% H₂O+40% H₂+N₂ and 3% H₂O+H₂ atmosphere are $3.67 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ and $5.44 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, respectively, at 1 173 K. Compared with reports mentioned above, BaZr_{0.76-x}Y_{0.2}Pr_xNi_{0.04}O_{3-δ} membranes exhibit its superior hydrogen permeability. However, the hydrogen permeability in mixed electron proton ceramic membranes is still inferior to the requirements of industrial processes. Therefore, the focal point of the next work is to further improve the proton conductivity of the hydrogen permeation membrane.

The hydrogen permeation process consists of two parts: the exchange process of gas on the membrane surface and the transport process of protons and electrons in the bulk phase. These two transport processes work together to affect the total hydrogen permeation rate^[75]. When the membrane thickness is thin, surface diffusion of hydrogen plays a dominant

Table 2 Hydrogen permeability comparison of ceramic and cermet membrane

Material	Temperature/ K	Permeability/ (mol·cm ⁻² ·s ⁻¹)	Reference
SrCe _{0.8} Yb _{0.2} O _{3-δ}	1 123	5.56×10^{-10}	[63]
Ni-SrCe _{0.8} Yb _{0.2} O _{3-δ}	1 173	2.12×10^{-9}	[63]
Nd _{5.5} WO _{12-δ}	1 130	2.4×10^{-10}	[64]
(La _{5/6} Nd _{1/6})WO _{12-δ}	1 173	3.49×10^{-10}	[65]
BaZr _{0.8} Y _{0.15} Mn _{0.05} O _{3-δ}	1 173	2.73×10^{-10}	[66]
La _{0.995} Ca _{0.005} NbO _{4-δ} -30% LaNb ₃ O ₉	1 243	1.75×10^{-10}	[67]
Ni-BaCe _{0.7} Zr _{0.1} Y _{0.2} O _{3-δ}	1 123	3.13×10^{-9}	[68]
Ni-BZPY	1 173	3.67×10^{-10}	[52]
Ni-BZPY	1 173	5.44×10^{-10}	[52]
SCY-SDC	1 173	1.21×10^{-7}	[69]
BaCo _{0.4} Fe _{0.4} Zr _{0.1} Y _{0.1} O _{3-δ}	1 223	5.06×10^{-7}	[70]
Ni-BZCYYb	1 123	5.43×10^{-7}	[71]
Ba(Zr _{0.1} Ce _{0.7} Y _{0.2})O _{3-δ}	1 173	1.71×10^{-7}	[72]
BaCe _{0.8} Y _{0.2} O _{3-δ}	1 173	2.53×10^{-7}	[73]
60(Ce _{0.85} Pr _{0.15} O _{2-δ})- 40(Pr _{0.6} Sr _{0.4} Fe _{0.9} Al _{0.1} O _{3-δ})	1 198	7.37×10^{-7}	[74]
BZYP10N4	1 173	2.60×10^{-8}	This work
BZYP5N4	1 173	1.75×10^{-8}	This work

role. Conversely, bulk diffusion controls the entire process^[75]. When the permeation process is controlled by bulk diffusion, the amount of hydrogen gas passing through the hydrogen separation membrane is related to the hydrogen partial pressure gradient on both sides of the membrane according to the Wagner^[76] equation, which can be expressed as:

$$J_{\text{H}_2} = \frac{RT}{4F^2L} \times \frac{\sigma_{\text{H}^+} \sigma_{\text{el}}}{\sigma_{\text{H}^+} + \sigma_{\text{el}}} \times \ln \frac{P'_{\text{H}_2}}{P''_{\text{H}_2}} \quad (4)$$

where, L is the thickness of the membrane; F is the Faraday constant; T is the temperature of the hydrogen permeation process; R is the gas constant; P'_{H_2} and P''_{H_2} are the hydrogen partial pressures on both sides of the membrane, respectively; σ_{H^+} is the proton conductivity; σ_{el} is the electronic conductivity.

When the electronic conductivity of the proton-electron mixed conductor is much greater than the proton conductivity, that is, $\sigma_{\text{H}^+} \ll \sigma_{\text{el}}$, the above Wagner equation can be simplified to:

$$J_{\text{H}_2} = \frac{RT}{4F^2L} \times \sigma_{\text{H}^+} \times \ln \frac{P'_{\text{H}_2}}{P''_{\text{H}_2}} \quad (5)$$

The proton conductivity of $\text{BaZr}_{0.76-x}\text{Y}_{0.2}\text{Pr}_x\text{Ni}_{0.04}\text{O}_{3-\delta}$ at different temperatures is calculated according to the simplified Wagner equation (5), and the results are shown in Fig. 6(b). The calculated proton conductivities of BZYN4, BZYP5N4 and BZYP10N4 at 1073 K are 8.38×10^{-4} , $3.51 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ and $7.85 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, respectively. Compared with the tested results, which are 3.01×10^{-3} , $1.55 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ and $1.93 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$, respectively, the calculated conductivities are slightly lower. Although BZYN4, BZYP5N4, and BZYP10N4 are dominated by proton conductivity, the transport of electrons and oxygen ions still contributes to some extent to the conductivity. In addition, interface polarization consumes part of the driving force in the process of hydrogen permeation, *i.e.*, the chemical potential difference of the membrane^[77]. Therefore, the calculated proton conductivity is lower than the tested

results.

The most significant problem of current proton conductors is the contradiction between material stability and proton conductivity, that is, stable proton conductor materials have low proton conductivity, while materials with high proton conductivity are usually not sufficiently chemically stable against carbon dioxide and water vapor. Therefore, to further investigate the chemical stability, the short-term stability of the $\text{BaZr}_{0.76-x}\text{Y}_{0.2}\text{Pr}_x\text{Ni}_{0.04}\text{O}_{3-\delta}$ membranes in a wet CO_2 -containing atmosphere was investigated. The J_{H_2} of $\text{BaZr}_{0.76-x}\text{Y}_{0.2}\text{Pr}_x\text{Ni}_{0.04}\text{O}_{3-\delta}$ membranes are stable in CO_2 -containing atmosphere, with only BZYP10N4 showing a slightly decrease, implying that the membranes possess good resistance to CO_2 . The structural stability of the perovskite crystal is determined by both the ionic radius and the electronegativity of dopants^[78]. As can be seen in Table 3, the changes in ionic radius and electronegativity of Pr^{3+} ion are greater than those of Y^{3+} ion compared to the Zr^{4+} in BaZrO_3 , which explains the relatively low stability of the BZYP10N4 samples with more Pr ion doping.

Table 3 Radius and electronegativity of doped ions

Doping element	Ionic radius/Å	Electronegativity (neutral atom)
Zr^{4+}	0.72	1.33
Y^{3+}	0.90	1.22
Pr^{3+}	0.99	1.10

Due to the presence of Pt coated on the surface, it is not feasible to conduct analysis of the surface structure changes of the sample after the stability test. Therefore, additional treatments were performed on the samples in boiling water and in CO_2 atmosphere at 973 K for 10 h, respectively, and the XRD patterns are shown in Fig. 7. Comparing with the BaZrO_3 standard (JCPDS 06-0399) PDF card, only two small impurity peaks caused by Y_2O_3 were observed. This indicates that the

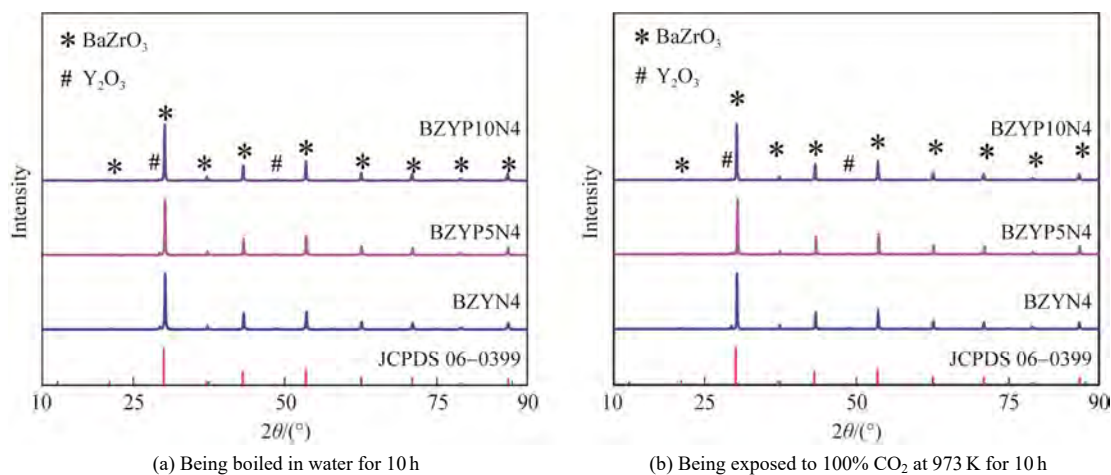


Fig. 7 XRD patterns after stability tests

Pr^{3+} and Ni^{2+} co-doped BZY still maintains a relatively intact phase structure even under the extreme environment. The stability of the phase structure after exposure to boiling water and CO_2 atmosphere suggests the potential durability of the membrane under practical application scenarios, enhancing its feasibility for hydrogen separation processes.

4 Conclusion

The $\text{BaZr}_{0.76-x}\text{Y}_{0.2}\text{Pr}_x\text{Ni}_{0.04}\text{O}_{3-\delta}$ ($x=0, 0.5, 0.1$) powders were synthesized using the sol-gel method, and the impact of co-doping of Pr^{3+} and Ni^{2+} on the electrochemical performances of BZY materials was analyzed. The X-ray diffraction results confirm the formation of a cubic perovskite structure in all samples, indicating successful doping of Pr^{3+} and Ni^{2+} ions into the BaZrO_3 lattice. The characterization using X-ray photoelectron spectroscopy, Raman spectroscopy, and electron paramagnetic resonance reveals that the introduction of Pr^{3+} leads to an increase in oxygen vacancy concentration. Additionally, due to the larger ionic radius of Pr^{3+} , grain growth is promoted, and the formation of a solid solution with Ni^{2+} further increases the grain size, resulting in improved electrical conductivity in BZYP10N4 compared to BZYP5N4. However, excessive Pr^{3+} doping causes a high concentration of oxygen vacancies, leading to defect association reactions and subsequently reducing the conductivity in BZYP10N4 at lower temperatures. Nevertheless, the hydrogen permeability shows a positive correlation with temperature, and the BZYP10N4 exhibits higher permeability compared to BZYP5N4, achieving a permeability of $2.60 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ at 1 173 K. The calculated proton conductivity slightly underestimates the experimental results due to the contribution of electron and oxygen ion transport to the electrical conductivity in BZY materials. Furthermore, short-term stability tests indicate that all samples exhibits good stability to CO_2 , signifying their potential as material for hydrogen separation membranes. Overall, the co-doping of Pr^{3+} and Ni^{2+} in BaZrO_3 demonstrates promising electrochemical properties, making it a prospective candidate for hydrogen separation membranes. Further research to optimize the proton conductivity while maintaining chemical stability would be crucial for the development of practical applications in the field of hydrogen separation technology.

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