LnBaCo2O5+δ

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Solid oxide fuel cells (SOFCs) represent a breed of eco-friendly, weather-independent, decentralized power generation technologies, distinguished for their broad fuel versatility and superior electricity generation efficiency.

Keywords: solid oxide fuel cells ; double perovskite ; oxygen

1. Physicochemical Properties of $LnBaCo_2O_{5+\delta}$

As depicted in **Figure 1**, the $LnBaCo_2O_{5+\delta}$ compound exhibits a perovskite structure of the 112 type. Relative to their disordered analogs, these orderly structures have been widely reported to considerably enhance the rate of oxygen transport [1][2]. Notably, Taskin et al. [1] were pioneers in observing a notably high oxygen diffusion coefficient (D_{chem}) of approximately 3.0×10^{-9} cm^2 s^{-1} at 350 °C and 10^{-5} cm^2 s^{-1} at 600 °C for the $GdBaCo_2O_{5+\delta}$ double perovskite. The oxygen transport characteristics of the $PrBaCo_2O_{5+\delta}$ double perovskite were subsequently evaluated by Kim et al. [3][4]. Their results demonstrated appreciably higher rates of oxygen transport (D_{chem}) for $PrBaCo_2O_{5+\delta}$ in comparison to $GdBaCo_2O_{5+\delta}$, suggesting an enhancement in oxygen transport properties corresponding to the increased size of the Ln cation. Tarancón et al. carried out a detailed comparative study between the double perovskite $LnBaCo_2O_{5+\delta}$ (Ln = Pr, Gd) and other classes of oxygen catalysts [5]. The double perovskite outperformed in terms of oxygen transport properties, emphasizing its considerable potential as a cutting-edge cathode material for SOFCs. It is important to recognize that significant variations exist in the $LnBaCo_2O_{5+\delta}$ oxygen tracer diffusion and the oxygen surface exchange coefficient as reported by different research groups [6]. Such disparities mainly stem from differences in the precise composition and/or microstructure of the samples used by distinct researchers.

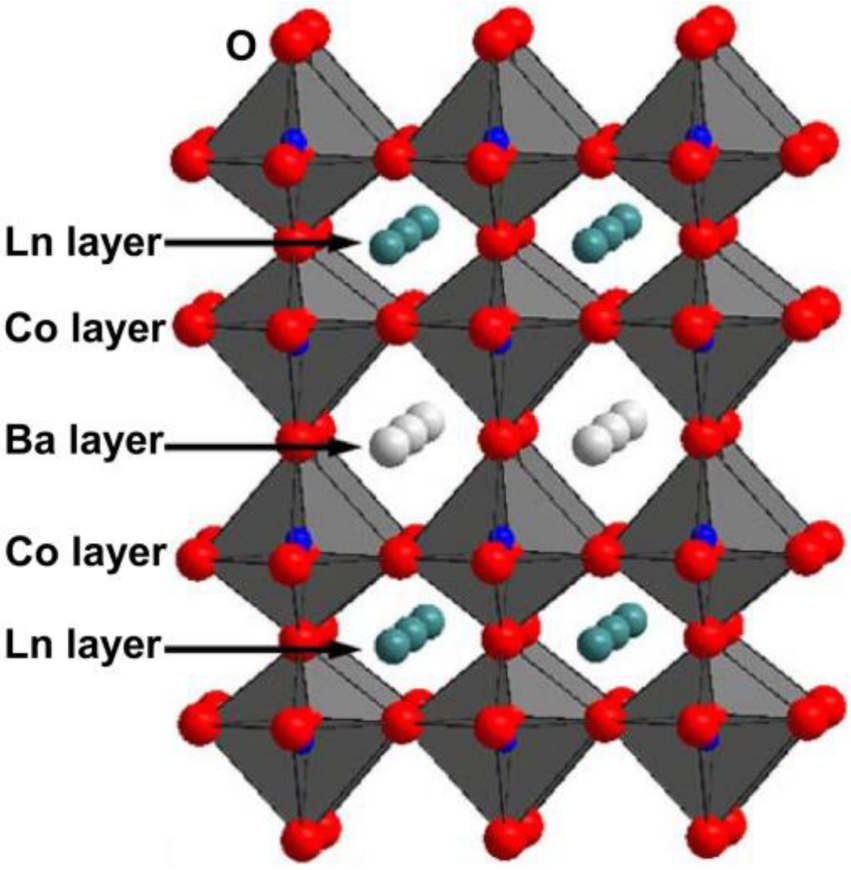

Figure 1. Schematic diagram of crystal structure for double perovskite oxide $LnBaCo_2O_{5+\delta}$.

Numerous experimental and theoretical studies have been undertaken to delve deeper into the oxygen diffusion behaviors in double perovskites [7][8][9][10][11][12][13][14][15][16][17][18][19][20][21][22][23][24][25]. Seymour et al. utilized static atomistic simulations based on the Born model to methodically examine the intrinsic defect processes of the double perovskite $LnBaCo_2O_{5.5}$ (Ln = Y, La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb) [7]. Their research indicated that the defect reaction with the lowest energy stemmed from the Ln/Ba antisite disorder energy, which diminishes with decreasing Ln size. This suggests that the ordered structure's primary foundation is the size difference between the Ln and Ba cations [7]. Parfitt et al. combined molecular dynamics with Born model potentials to study the oxygen transport behavior of $GdBaCo_2O_{5+\delta}$ at 900 K [8][9]. They posited that A-site cation ordering, in contrast to its disordered equivalent, can amplify oxygen bulk diffusivity while decreasing transport in the c-axis direction [8][9]. Importantly, the distinctively anisotropic oxygen diffusion in the double perovskite $GdBaCo_2O_{5+\delta}$ takes place exclusively within the [GdO_δ] and adjacent [CoO_2] layers. Shiiba et al. probed the distribution of oxygen vacancies in $GdBaCo_2O_{5+\delta}$ under various oxygen vacancy concentrations ($0 \le \delta \le 1$) and temperatures using a fusion of density functional theory and Monte Carlo simulation [11]. Their analysis showed that oxygen vacancies, which function as oxygen ion carriers, are restricted to the [GdO_δ] and neighboring [CoO_2] layers, reinforcing the anisotropic oxygen diffusion mechanism. Seymour et al. performed theoretical investigations on the oxygen transport properties of layered $PrBaCo_2O_{5+\delta}$ at 650 and 1000 °C, employing the MD method [13][14][15][16]. These proposed mechanisms for oxygen conducting were later confirmed experimentally via in situ high-temperature neutron powder diffraction and isotope exchange depth profile methods [13][14][15][16]. Additionally, it has been shown that $PrBaCo_2O_{5+\delta}$ has a lower energy barrier for oxygen diffusion perpendicular to the c-axis compared to Nd, suggesting enhanced oxygen ion diffusivity with larger Ln sizes [7][13]. Wang et al. detected rapid cobalt redox reactions in epitaxial $LaBaCo_2O_{5+\delta}$ within a temperature bracket of 260–700 °C, intimately tied to the processes of oxygen release and uptake processes [26]. This finding hints at the potential application of these films in SOFC cathodes. Notably, Wang et al. found the cobalt oxidation in the epitaxial thin films to be substantially swifter than the reduction process, denoting a more rapid oxygen uptake compared to the oxygen release [26]. Bao et al.'s research further revealed a layer-by-layer oxygen transport mechanism in epitaxial double perovskites, specifically $LnBaCo_2O_{5+\delta}$ (Ln = Pr, Er), which likely originates in their intrinsic anisotropic oxygen diffusion properties [27].

$LnBaCo_2O_{5+\delta}$, owing to its exceptionally promising properties, has been extensively studied as a cathode material for SOFCs [28][29][30][31][32][33][34][35][36][37][38]. Researchers have undertaken thorough studies into the structural performance, thermal expansion behavior, electrical conductivity, and electrochemical performance of these double perovskites. Studies on ions such as La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, and Gd^{3+} have shown that these oxides exhibit good chemical compatibility with commonly used electrolytes, including GDC, $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ (LSGM), and samarium oxide-doped ceria (SDC), at temperatures below 1000 °C [29][30][31][39]. After firing $LnBaCo_2O_{5+\delta}$ double perovskites at 850 °C in air for durations ranging from 60 to 100 h, no impurity phases or phase transitions were detected. This finding highlights the remarkable structural stability of these oxides under the standard operating conditions of SOFCs [28][32]. Additionally, the electrical conductivities of $LnBaCo_2O_{5+\delta}$ compounds tend to increase with growth in the size of the Ln ion, leading to a rise in the number of electronic holes created by interstitial oxygen [30][31]. The electrical conductivity values of these materials surpass 100 S cm^{-1} between 100 and 800 °C in air, meeting the electrical conductivity requirements for SOFC cathodes [28][30][31][32]. What is more, oxides with larger Ln ions exhibit superior electrochemical performance, stemming from enhanced oxygen transport and exchange rates [28][30]. For instance, as the Ln ion shifts from Gd^{3+} to La^{3+}, the maximum power density (PPD) values of SOFCs utilizing these double perovskite cathodes increase from 443 to 516 mW cm^2 [30].

Despite the numerous advantages of $LnBaCo_2O_{5+\delta}$ as a cathode catalyst for SOFCs, there are certain technical challenges that require further improvements. Firstly, enhancing the catalytic activity of these oxides for ORR is paramount. Chen et al. [29] observed that the ASR of $PrBaCo_2O_{5+\delta}$ on SDC electrolytes increases from 0.18 to 5.68 Ω cm^2 as the temperature drops from 650 to 500 °C. Moreover, the PPD of SOFCs utilizing $PrBaCo_2O_{5+\delta}$ as the cathode material decreases from 866 mW cm^2 (at 650 °C) to 115 mW cm^2 (at 500 °C). Secondly, it is essential to minimize the thermal mismatch between these cobalt-based cathode materials and other SOFC components. Kim et al. [30] reported that the thermal expansion coefficients (TECs) of $LnBaCo_2O_{5+\delta}$ double perovskites increase from 16.6×10^{-6} K^{-1} (Ln = Gd^{3+}) to 24.3×10^{-6} K^{-1} (Ln = Pr^{3+}) with larger Ln sizes at 80–900 °C. Given that the TECs of standard electrolytes for SOFCs, such as GDC, SDC, and LSGM, are around 11×10^{-6} K^{-1}, this notable thermal mismatch between $LnBaCo_2O_{5+\delta}$ and the electrolyte could adversely affect fuel cell stability. Thirdly, tuning the physicochemical properties of the surface is essential. The surface physicochemical properties serving as catalysts for the ORR significantly influence cathode performance. Findings by Téllez et al. [34] suggest that the surface composition and morphology of $LnBaCo_2O_{5+\delta}$ (Ln = Pr, Gd) double perovskites are profoundly influenced by exposure time, temperature, and ambient atmosphere. A quick covering of the electrocatalytic transition metal by inactive Ln^{3+} or Ba^{2+} cations, observed under certain conditions, can be detrimental to the ORR. Therefore, the subsequent sections will provide a comprehensive overview of advancements in

studying the physicochemical property attributes of double perovskites and in adjusting the composition and nanostructure of $LnBaCo_2O_{5+\delta}$.

2. Nanostructure and Nanoscience of $LnBaCo_2O_{5+\delta}$

Nanostructures offer significantly enhanced surface area-to-volume ratios and expanded interphase and interfacial areas. As such, they have the potential to augment electrochemical reaction sites. Perovskite oxides with nanostructured morphologies have been rigorously studied and employed in solid oxide fuel cells [40][41][42][43][44][45][46][47][48][49][50][51][52][53][54][55][56] as well as other energy-related applications [57][58][59][60]. Reducing the operating temperature creates an opportunity to use nanostructured materials, which can sidestep the slow ORR and, in turn, boost the catalytic performance of the cathode [40][41][42][43][44][45][46][47][48][49][50][51][52][53][54][55][56]. Infiltration is a common and straightforward method for developing nanostructured cathode materials tailored for SOFCs [40][41][42]. A nanostructured cathode material, represented by the formula $SmBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$, was created by infusing its precursor solution into the porous LSGM framework, followed by calcining at 850 °C. This material showcased commendable electrochemical performance [43]. For instance, it showed an ASR as low as 0.12 Ω cm^2 and a PPD of up to 0.70 W cm^{-2} at 500 °C. Electrospinning, praised for its scalability and precision, was utilized to fabricate a $GdBaCo_2O_{5+\delta}$ cathode material possessing a nanofiber configuration, achieving a comparatively low ASR, approximately 0.10 Ω cm^2 at 700 °C [52].

Ding et al. [43] managed to produce unique needle-like nanospikes of the cathode material $PrBaCo_2O_{5+\delta}$ by applying a discharge voltage of 0.1 V to the anode-supported single cell, arranged as NiO-$Sm_{0.2}Ce_{0.8}O_{1.9}$/$Sm_{0.2}Ce_{0.8}O_{1.9}$/$PrBaCo_2O_{5+\delta}$, and then firing the $PrBaCo_2O_{5+\delta}$ cathode slurry at 450 °C. These nanospikes, with an average diameter of 20 nm and lengths spanning from tens to hundreds of nanometers, are uniformly distributed along the pore boundaries of the porous cathode. For the single cell that used the nanospikes $PrBaCo_2O_{5+\delta}$ as the cathode, exceptionally high maximum power densities of 1.453 W cm^{-2} at 550 °C and 1.044 W cm^{-2} at 500 °C, coupled with excellent endurance, were recorded.

The fabrication of double perovskites in a thin-film architecture not only facilitates fundamental studies to evaluate inherent properties of materials [27][41][61][62] but also illuminates a new avenue for the development of high-performing cathode materials [26][44][46]. The influence of orientations on the electrochemical performance of double perovskites was appraised by Gao et al. [44]. They produced $PrBaCo_2O_{5+\delta}$ thin films with different orientations, including (110), (001), and (111), using pulsed laser deposition. The thin film with the (111) orientation showed superior performance, achieving an ASR of 0.302 Ω cm^2 at 600 °C. Liu et al. [45][46] fabricated symmetric half-cells by coupling single-crystal, highly epitaxial $LnBaCo_2O_{5+\delta}$ (Ln = Pr, La) thin-film cathodes with $Gd_{0.8}Ce_{0.2}O_2$:$Y_{0.08}Zr_{0.92}O_2$ electrolytes and subsequently characterized their oxygen surface exchange and catalytic activity. For instance, the symmetric half-cell featuring the epitaxial $LaBaCo_2O_{5+\delta}$ thin film displayed remarkable properties, such as an impressively fast surface exchange rate of 0.017 cm s^{-1} at 600 °C and an exceptionally low activation energy value of 0.49 eV. These outcomes might be ascribed to the structural entropy arising from the nano-ordered oxygen vacancy framework.

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