

Article

Characteristic Influence of Cerium Ratio on PrMn Perovskite-Based Cathodes for Solid Oxide Fuel Cells

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Abstract

In this study, cerium with different ratios ($x = 0$ (zero), 0.1, 0.15, 0.5) was added to the PrMn structure as an A-site material to evaluate characteristic behavior as a potential cathode material for solid oxide fuel cells. The $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ electrocatalysts were synthesized using the sol-gel combustion method and were assessed for their electrochemical, phase, and structural properties, as well as desorption and reducibility capabilities. Phase changes, from orthorhombic to cubic structures observed upon cerium additions, were evaluated via the X-Ray diffraction method. X-Ray photoelectron spectroscopy (XPS) showed the valence states of the surface between the $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Pr}^{4+}/\text{Pr}^{3+}$ redox pairs, while oxygen temperature programmed desorption (O_2 -TPD) analysis was used to evaluate the oxygen adsorption and desorption behavior of the electrocatalysts. Redox characterization, evaluated via hydrogen atmosphere temperature-programmed reduction (H_2 -TPR), revealed that a higher cerium ratio in the structure lowered the reduction temperature, suggesting a better dynamic oxygen exchange capability at a lower temperature for the $\text{Pr}_{0.5}\text{Ce}_{0.5}\text{MnO}_{3-\delta}$ catalyst compared to the electrochemical behavior analysis by the electrochemical impedance spectroscopy method. Moreover, the symmetrical cell tests with $\text{Pr}_{0.5}\text{Ce}_{0.5}\text{MnO}_{3-\delta}$ electrodes showed that, when combined with scandia-stabilized zirconia (ScSZ) electrolyte, the overall polarization resistance was reduced by approximately 28% at 800 °C compared to cells with yttria-stabilized zirconia (YSZ) electrolyte.

Keywords: solid oxide fuel cell; scandia-stabilized zirconia; praseodymium catalyst; PrCeMn; cathode; electrolyte comparison



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1. Introduction

To overcome successive climatic and political challenges, the shift toward alternative energy sources has gained significant momentum [1]. Among these alternatives, fuel cells have attracted considerable attention due to their low-emission/emission-free operation and highly efficient electrical conversion capabilities. Solid oxide fuel cells (SOFCs), in particular, stand out for their high performance at elevated temperatures (~1000 °C), offering fuel flexibility and superior efficiency compared with other fuel cell types. However, reducing their operating temperatures is essential to mitigate issues such as decreased material strength and the high costs associated with high-temperature operations, thereby improving overall system efficiency. To achieve this, modifications to the SOFC electrodes and electrolytes are required to minimize performance degradation and maintain oxygen

reduction reaction (ORR) activity, which can result from the reduced kinetic energy at lower temperatures [2–4].

Materials exhibiting mixed ionic and electronic conduction (MIEC) can enhance the performance of SOFCs. The selection of appropriate cathode materials with optimal electrical and ionic conductivity is essential to sustain the oxygen reduction reaction activity and reduce the increased polarization resistance typically associated with lower operating temperatures [3,5]. Many perovskite structures, such as double perovskites [6], A-site-ordered double perovskites [7,8], and Ruddlesden–Popper phases [9], have been studied over the years as promising electrocatalysts for SOFCs. A combination of A-site as a rare-earth or an alkali-earth element and B-site as typically a transition metal in perovskites can result in different conductivity mechanisms to maintain charge neutrality in the geometric relationship [7]. In the ionic compensation mechanism, ionic conductivity occurs through the formation and movement of oxygen vacancies. Moreover, B-site (e.g., $\text{Mn}^{3+}/\text{Mn}^{4+}$) is usually associated with electronic compensation, since the redox properties of B^+ cations (e.g., $\text{Mn}^{3+}/\text{Mn}^{4+}$) directly affect electronic conductivity [10,11].

Cerium is widely used as a material for intermediate-temperature SOFC electrolytes and is known for its high conductivity [12,13]. However, the main limitation of CeO_2 -based electrolytes is the reduction of Ce^{4+} to Ce^{3+} in reducing atmospheres, which decreases ionic transfer and causes electronic leakage at the cell, a desirable property for a MIEC material as a cathode electrode [14]. As in the oxidizing atmosphere, cerium exhibits oxygen mobility due to $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox reactions, and when combined with praseodymium on the structure, oxygen vacancy can be enhanced in $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{3-\delta}$ as both ions' similar size oxygen mobility increased [15,16]. The variable valence states of Pr ($\text{Pr}^{3+}/\text{Pr}^{4+}$) can also increase oxygen vacancies and electronic conductivity. At low Pr concentration ($x \leq 0.1$), $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{3-\delta}$ shows the temperature-dependent conductivity similar to Gd-doped cerium, indicating that it behaves as an ionic conductor at high temperatures [13,17]. However, Pr-doped Ce electrocatalysts also have relatively large thermal expansion coefficients (TECs) at higher temperatures, which occur due to oxygen vacancy formation associated with Pr reduction [13,18].

Manganite-based materials are widely considered for cathodes for Zirconia-based electrolytes due to their similar thermal expansion coefficient (TEC) and high electrical conductivity, which are essential for the cathode material [19]. Incorporation of Mn into perovskite structures often forms an orthorhombic crystal structure due to the Mn^{3+} orbital characteristic [19,20]. Perovskite-type structures, when doped with Pr at the A-site and Mn at the B-site, have been reported to exhibit lower over potentials as well as improved performance at intermediate temperatures [21]. Accordingly, the present study investigates a series of compositions of Pr and Ce in $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ ($x = 1, 0.9, 0.85, 0.5$; hereafter denoted as C1, C9, C8, and C5, respectively) combined with Mn as a B-site cation in a novel perovskite.

Although many cathode electrodes have been investigated for solid oxide fuel cells, a significant challenge remains in addressing the polarization resistance encountered at intermediate temperatures between the electrode and the electrolyte, which limits overall efficiency and performance. Electrolytes must possess good oxygen ion conductivity, high chemical stability, low electronic conductivity, and acceptable mechanical properties to be compatible with electrode materials as well. YSZ is an oxygen ion conductor and has been widely used in SOFCs, which shows high chemical and mechanical strength and stability [22]. However, YSZ requires high temperatures ($>800^\circ\text{C}$) to achieve good performance in an electrolyte-supported cell, which makes it susceptible to system-related failures [23]. Although zirconia remains the preferred electrolyte material for SOFCs, scandia-stabilized zirconia shows potential for lower operating temperatures and enhanced

conductivity [24]. Studies have shown that when ScSZ is used as the electrolyte, intermediate operating temperatures of 600–800 °C can be achieved on SOFCs [25]. In this context, the present study evaluates both $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ compositions in symmetrical cells using both yttria-stabilized zirconia and scandia-stabilized zirconia electrolytes. This study aims to investigate the ion conduction behavior of Pr and Ce on the Perovskite structure, which is coupled with Manganese as a B-site transient metal. While the experiments in the paper mainly focus on ScSZ electrolyte, the comparison between the YSZ electrolyte conducted with the promising electrocatalysts emphasizes the differences between the electrolytes. The comparative electrochemical impedance spectroscopy (EIS) analysis revealed that $\text{Pr}_{0.5}\text{Ce}_{0.5}\text{MnO}_{3-\delta}$ (C5) exhibits the most favorable behavior at low temperature than all electrocatalysts and can achieve a 28% reduction in polarization resistance at 800 °C with ScSZ compared to YSZ. Overall, the study provides an understanding of characteristic behaviors, including phase and structural changes, oxygen vacancy formation, and redox dynamics, which were obtained using advanced characterization techniques such as XRD, XPS, TPR, and TPD, and their influence on electrochemical results obtained by EIS analysis on PrCeMn-based electrodes.

2. Results and Discussion

2.1. Results of X-Ray Diffraction Analysis

After calcination, the prepared electrocatalysts were analyzed to evaluate the structural properties using X-Ray diffraction (XRD). Figure 1 shows the result of the diffraction patterns of the synthesized $\text{PrMnO}_{3-\delta}$ (C1) and $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ (C5, C8, C9) electrocatalysts. In the diffraction pattern of $\text{PrMnO}_{3-\delta}$ (C1), PrMnO_3 was primarily identified with an orthorhombic structural phase in the Pnma space group, while additional minor peaks from Pr_2O_3 and Mn_2O_3 were detected, indicating a multiphase composition. The effect of cerium addition on the structure can be observed in Figure 1 as a shift towards PrMn_2O_5 -type phases, as well as in the Pnma space group with orthorhombic structure, in the diffraction patterns of the cerium-containing electrocatalysts. The shift from PrMnO_3 (C1) to PrMn_2O_5 (C5, C8, C9) generates the mixed ionic states of $\text{Mn}^{3+}/\text{M}^{4+}$ in Ce-containing electrocatalysts [26], as evidenced by a noticeable increase in peak intensity from C9 catalyst to C5 in Figure 1.

Phase analysis of the electrocatalysts revealed the presence of Pr-Ce-O phases with the intended concentration ratios of Pr/Ce, which are, respectively, the $\text{Pr}_{0.5}\text{Ce}_{0.5}\text{O}_2$ phase (04-018-7331 reference code) for C5; $\text{Pr}_{0.8}\text{Ce}_{0.2}\text{O}_2$ (01-080-4843 reference code) for C8; and the $\text{Pr}_{0.9}\text{Ce}_{0.1}\text{O}_2$ phase (01-080-4846 reference code) for C9, with all exhibiting cubic crystal structures in the Fm3m space group. Multiple phases can also be observed in the C5, C8, and C9 patterns, including smaller amount of Pr_6O_{11} and CeO_2 , indicating the presence of mixed valence of Pr ions and Ce^{4+} ions. The formation of Pr_6O_{11} phases, due to their mixed valence states [27], may contribute to enhanced oxygen vacancy concentration in the catalyst, as reported by Borchert et al. [28]. The phase observation can be examined through the shift from the Pr_2O_3 phase to the Pr_6O_{11} phase, which is associated with the presence of $\text{Pr}^{3+}/\text{Pr}^{4+}$ states in the structure [29,30].

Phase shifts in the XRD patterns and changes in intensity between 25° and 35° further suggest that the addition of cerium may have contributed to changes in the bonding structure, leading to the formation of the Pr-Ce-Mn-O phase.

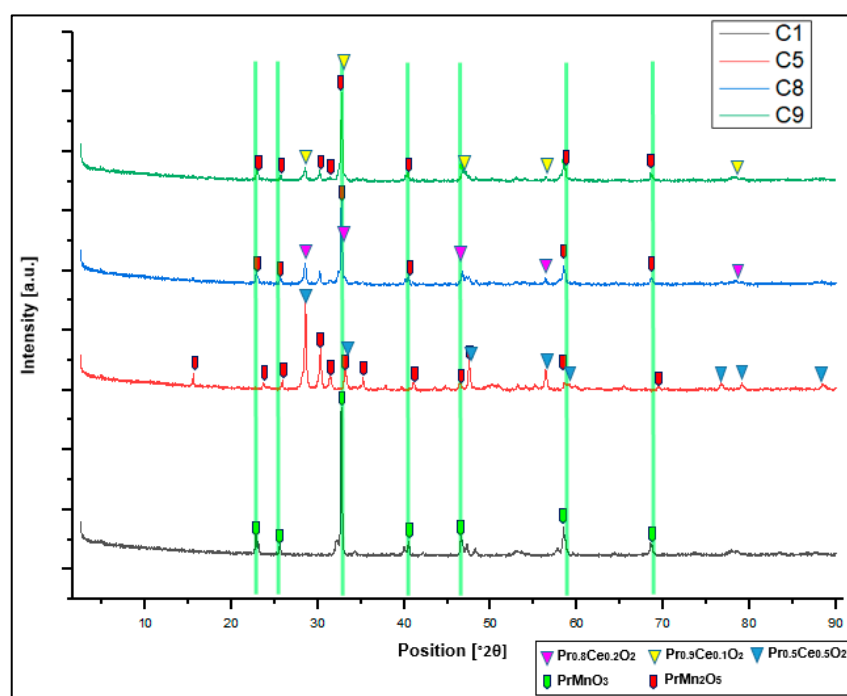


Figure 1. XRD patterns of synthesized C1, C5, C8, and C9 electrocatalyst powders.

2.2. Results of X-Ray Photoelectron Spectroscopy

The surface composition of the prepared $\text{PrMnO}_{3-\delta}$ and $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ electrocatalysts was analyzed using XPS measurements in the binding energy (BE) regions between 520 and 970 eV after calcination. The characteristic spectra for Pr3d, Ce3d, Mn2p, and O1s of each prepared catalyst are shown in Figure 2, within these BE regions.

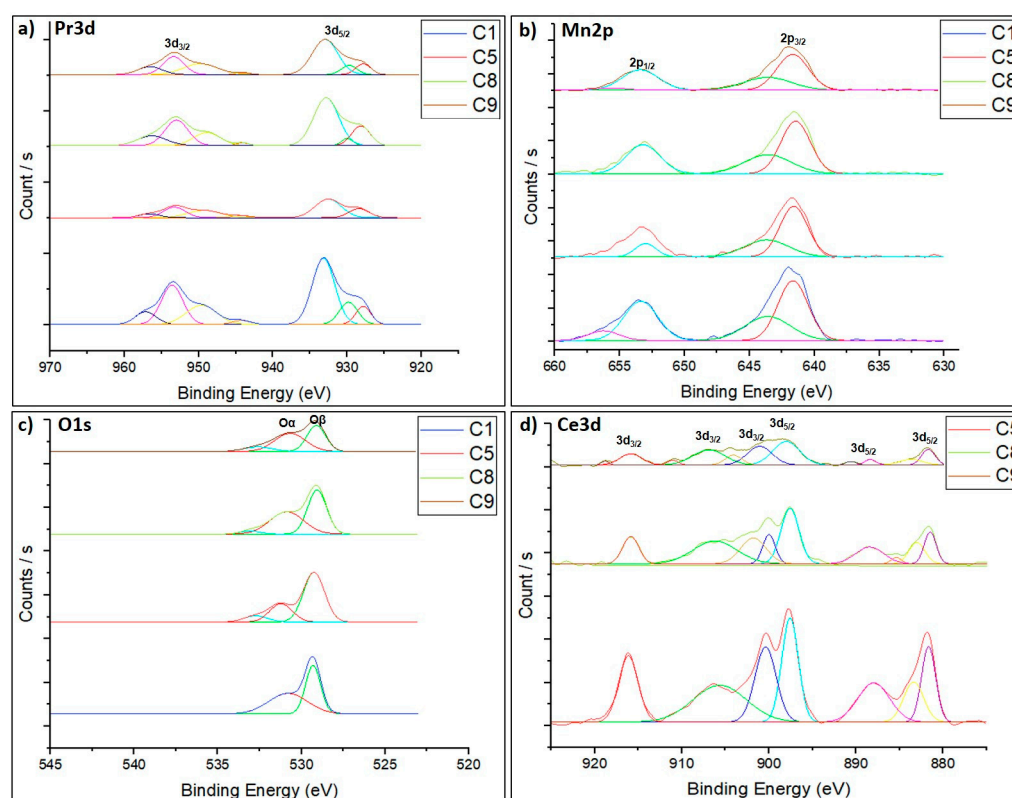


Figure 2. Comparative XPS spectrum of (a) Pr3d, (b) Mn2p, (c) O1s, and (d) Ce3d orbitals.

At the XPS spectra for the Ce3d region, the observed peaks correspond to the valence states of Ce^{3+} and Ce^{4+} species, each represented by a pair of the spin–orbit components (doublet peak) at $3d_{3/2}$ and $3d_{5/2}$. The characteristic oxidation state of Ce^{4+} ($3d_{3/2}$) species is evident for C5, C8, and C9 with binding energies of 916.1/900.2, 915.9/899.9, and 915.7/901.1 eV, respectively, accompanied by corresponding doublet peaks ($3d_{5/2}$) at 897.7/881.7, 897.5/881.4, and 898.3/881.6 eV. The peak intensity increases, and the peaks become more distinct as the cerium ratio increases, indicating the surface composition of Ce^{4+} with characteristic peaks for cerium-containing electrocatalysts [15,31]. The areas were deconvoluted using Gaussian fitting, and the percentages of Ce^{4+} content are observed to be 71%, 77%, and 86% for C5, C8, and C9 catalysts, respectively. The results demonstrate that increasing the cerium content promotes the formation of Ce^{3+} species, which is a phenomenon that has been associated with an increased formation of oxygen vacancy as reported in the literature [32,33].

Similarly, to the XPS characteristic of the orbital splitting of Ce^{4+} , doublet peaks can be observed for $\text{Pr}^{3+/4+}$ in Figure 2a, indicating their coexistence in the structure. The oxidation states for $\text{Pr}3d_{3/2}$ were observed at 953.6, 953.3, 953.1, and 953.3 eV for C1, C9, C8, and C5, respectively, and $\text{Pr}3d_{5/2}$ at 933.1, 932.9, 932.8, and 932. eV, which is the characteristic peak of Pr^{3+} . The peak area composition of $\text{Pr}^{3+}/\text{Pr}^{4+}$ obtained from deconvolution (Table 1) indicated higher concentration of Pr^{3+} species at the surface [15,34].

Table 1. Percentage contributions of $\text{Pr}^{3+}/\text{Pr}^{4+}$, $\text{Ce}^{3+}/\text{Ce}^{4+}$, and $\text{Mn}^{3+}/\text{Mn}^{4+}$ valence states and the $\text{O}_\alpha/\text{O}_\beta$ ratio from XPS analysis.

%	Pr3d		Ce3d		Mn2p		O1s
	Pr^{4+}	Pr^{3+}	Ce^{4+}	Ce^{3+}	Mn^{4+}	Mn^{3+}	$\text{O}_\alpha/\text{O}_\beta$
C1	23	77			31	69	0.9
C9	18	82	86	12	26	74	4.3
C8	21	79	77	23	30	70	12
C5	22	78	71	29	23	76	2.8

The XPS spectra of Mn2p show two distinguished peak regions (Figure 2b) that represent the doublet of $\text{Mn}2p_{3/2}$ and $\text{Mn}2p_{1/2}$, respectively, at 641 and 653 eV binding regions caused by the core hole spin–orbit coupling [35], with a separation of the signals about 12 eV indicating different oxidation states [36]. Deconvolution of the peaks has indicated mixed valence states of the Mn^{4+} and Mn^{3+} species, as given in Table 1, with doublet peaks, which give rise to the asymmetric peak shapes. Multiple structures represent spin–orbit splitting. Strong peaks at 641.4–641.7 eV and concentration valence states represent the dominance of the Mn^{3+} ions on the electrocatalysts' surfaces [35].

Two major peaks are observed for the O1s shown in Figure 2c, representing different features of oxygen, such as the absorbed oxygen species (O_α) and lattice oxygen (O_β) [37–39]. Two kinds of absorbed oxygen can be identified for C5, C8, and C9 electrocatalysts. The surface oxygen ($\text{O}_{\alpha1}$) adsorbed on the oxygen vacancies can be observed for C1, C9, C8, and C5, respectively, at 530.8, 530.4, 530.9, and 531.2 eV while the binding energies of the C9, C8, and C5, respectively, at 532.6, 533, and 532.7 are broader and represent hydroxyl groups and absorbed water species ($\text{O}_{\alpha2}$) on the surface. The lattice oxygen (O_β) can be observed between 527 and 530 eV, with each peak listed in Table 1 for individual electrocatalysts [35].

2.3. Results of Temperature Programmed Reduction (H_2 -TPR)

The reduction behaviors of the electrocatalyst were examined through temperature-programmed H_2 reduction reactions, as shown in Figure 3. Cruz-Pacheco et al., 2019,

demonstrated that the surface oxygen reduction of Ce^{4+} occurs at 505 °C, and the first peak at 490 °C in Figure 3 for C5 can be identified as corresponding to that process [15].

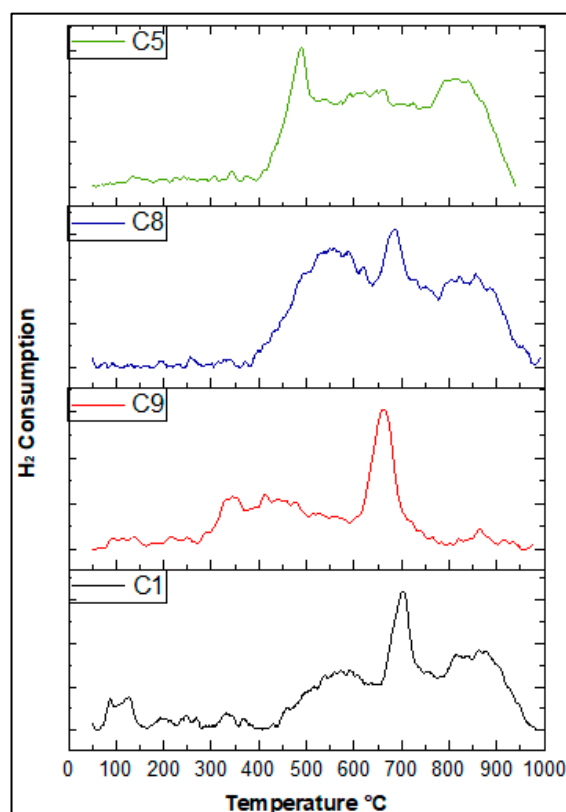


Figure 3. H_2 TPR profiles of prepared electrocatalysts.

Multiple reduction steps are observed in Figure 3 for all prepared electrocatalysts. The three major reduction profiles are shifted and change in intensity with cerium addition to the structure, indicating a change in the phases and reduction capabilities. Similar reduction steps with the three major peaks occurred between 400 °C and 950 °C for all catalysts. Adding cerium to the structure shifted the first reduction peak at 577 °C for C1 to lower temperatures at 500 °C for C5, while the intensity of the second reduction peak at 700 °C decreased from C1 to C5. Following the C9 catalyst TPR profile, the second major reduction step appeared as the only significant peak, while the remaining peaks exhibited low intensities. The Mn^{4+} species in perovskite structures are typically known to be reduced within the 300–400 °C range due to low cation coordination number [40]. In the TPR profile of C9, the reduction of Mn^{4+} begins at a lower temperature, whereas with increasing cerium content, the onset temperature for Mn^{4+} reduction shifts to 400 °C and above. The addition of 10% cerium into the C9 catalyst structure may have caused structural changes, thereby lowering its reduction capabilities compared to other catalysts. As observed in the XRD and XPS analyses, the addition of cerium to the structure promoted a shift from Mn^{3+} to Mn^{4+} ionic states, influencing the lower reduction temperature peaks in the TPR profile from C1 to C5 by increasing the redox capability.

2.4. Oxygen Temperature-Programmed Desorption (O_2 -TPD)

Oxygen temperature-programmed desorption analyses provide information about the temperature-dependent oxygen evaluation of the electrocatalysts. Figure 4 displays the desorption graphs, obtained by mass spectrometry, for the electrocatalysts with various Pr:Ce ratios.

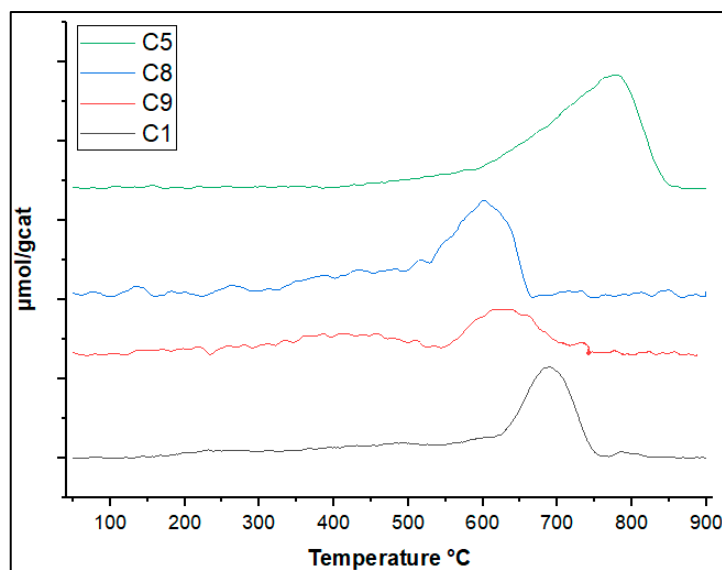


Figure 4. Desorption profile of $\text{Pr}_{1-x}\text{Ce}_x\text{MnO}_{3-\delta}$ electrocatalysts versus temperature.

The temperature-dependent oxygen adsorption and desorption behavior of the electrocatalyst was evaluated using O_2 -TPD measurements. In the desorption profiles in Figure 4, a broad spectrum was observed, with only one clear desorption peak appearing between 500 and 850 °C, corresponding to the release of bulk oxygen (β -oxygen). Therefore, β -oxygen desorption reflects oxygen mobility in the PrCeMn electrocatalyst, involving oxygen exchange between the bulk oxygen and surface oxygen vacancies [41,42]. Furthermore, the addition of cerium to the $\text{PrMnO}_{3-\delta}$ structure reduced the temperature by shifting the peak at 700 °C for C1 to 600 °C for C8, indicating enhanced oxygen mobility at lower temperatures.

The highest intensity of the peaks from the desorption profiles in Figure 4 was observed at the C5 catalyst, which has the highest cerium ratio of 50:50 (Pr:Ce). By reducing the cerium to 0.1, the peak intensity decreased dramatically, as can be observed for the C9 electrocatalyst with a 90:10 Pr:Ce ratio.

2.5. Results of Electrochemical Impedance Spectroscopy Analysis of Symmetrical Cells

The analyzed impedance curves of the symmetrical cells are presented in Figure 5, measured between 700 and 850 °C at open-circuit voltage in an air atmosphere. To make the comparison more comprehensible, all impedance data were adjusted so that the plots start from zero on the real axis. The impedance spectra show a low-resistance arc in the high-frequency region and a main high-resistance arc in the mid-frequency region, with the two arcs more or less overlapping. The sum of these two arcs is defined as R_{ASR} , which represents the overall polarization resistance of the system with a 0.22 cm² interfacial geometric area.

Relatively higher polarization resistances are observed for C1 and C9 catalysts at 700–750 °C, compared to C8 and C5; however, their performance significantly increases at higher temperatures. Increasing the cerium ratio in the perovskite structure lowers the resistance at lower temperatures; however, structural distortions can be observed at high temperatures, as shown in Figure 5c,b, with the formation of a second peak. However, the best performance was achieved by C5 at 800 °C, with a resistance of $4.75 \pm 0.25 \, \Omega \cdot \text{cm}^2$, and C5 showed the lowest resistance compared to the other electrocatalysts.

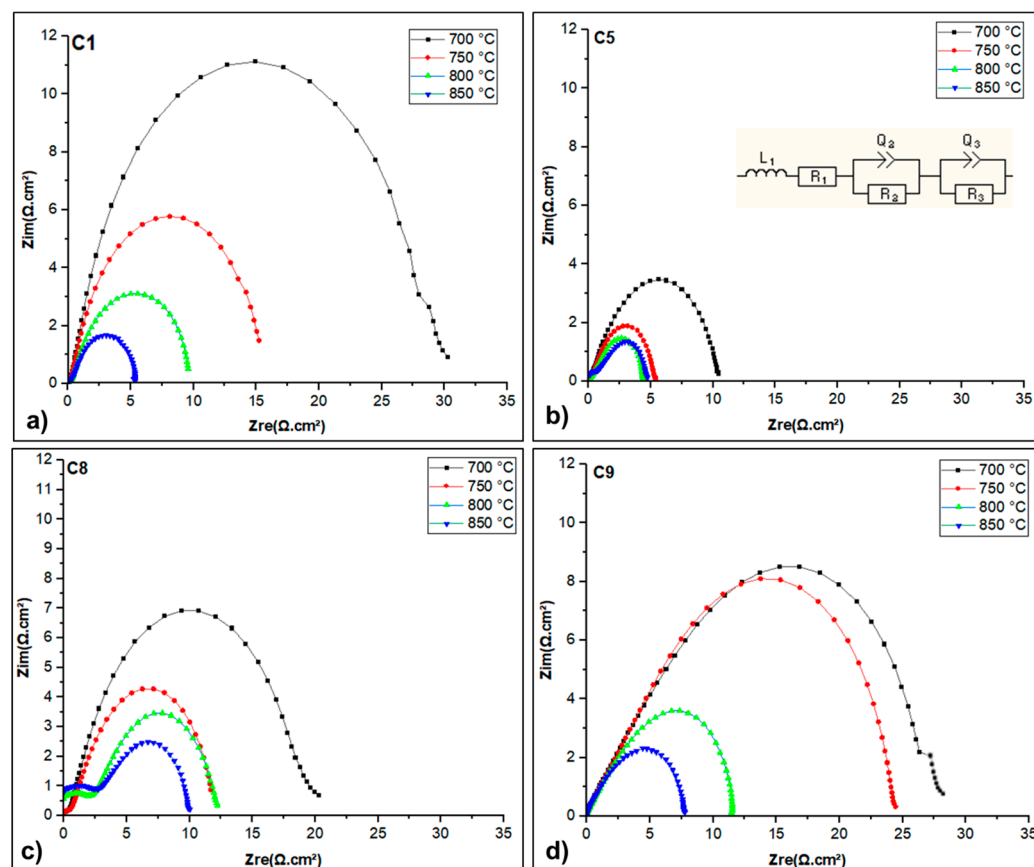


Figure 5. Impedance profiles of symmetrical cells in dry air environment; (a) C1, (b) C5, (c) C8, and (d) C9.

In order to observe the ORR activation with electrode impedance characteristics, the data were fitted using $L_1R_1(R_2/Q_2)(R_3Q_3)$ equivalent circuit where L stands for inductance caused by electrical connection, R_1 for ohmic resistance of electrolyte, and R_iQ_i for two distinguished polarization resistance at high and mid frequency where extent of depression in a semicircular arc, due to distribution in the relaxation time constant, indicates the constant phase element as Q [43,44].

The fitting results obtained from the equivalent circuit analysis are summarized in Table 2, which shows parameters including R_1 , R_2 , R_3 , and the total resistance R_{ASR} , as well as a parameter indicating the similarity between Q and the true capacitor for each sample and temperature. The capacitance value of the circuits is calculated using Equation (1) [45].

Table 2. Fitted results of $L_1R_1(R_2/Q_2)(R_3Q_3)$ equivalent circuit.

		R_1 ($\Omega \cdot \text{cm}^2$)	R_2 ($\Omega \cdot \text{cm}^2$)	a_2	R_3 ($\Omega \cdot \text{cm}^2$)	a_3	R_{ASR} ($\Omega \cdot \text{cm}^2$)
C1	700 °C	2.3	0.46	0.49	29.04	0.85	29.5
	750 °C	1.8	0.27	0.64	15.55	0.82	15.83
	800 °C	2.09	0.26	0.81	9.764	0.72	10.03
	850 °C	1.65	0.45	0.58	5.072	0.74	5.52
C9	700 °C	2.8	4.45	0.56	24.55	0.74	29.00
	750 °C	1.85	4.22	0.57	20.51	0.81	24.73
	800 °C	1.3	2.58	0.60	9.28	0.79	11.85
	850 °C	1.115	0.94	0.71	6.99	0.72	7.93

Table 2. Cont.

		R1 ($\Omega \cdot \text{cm}^2$)	R2 ($\Omega \cdot \text{cm}^2$)	a2	R3 ($\Omega \cdot \text{cm}^2$)	a3	R _{ASR} ($\Omega \cdot \text{cm}^2$)
C8	700 °C	4.00	0.54	0.71	19.26	0.79	19.80
	750 °C	3.38	1.05	0.45	11.16	0.82	12.21
	800 °C	5.52	2.28	0.74	10.28	0.73	12.56
	850 °C	5.24	2.46	0.87	8.04	0.67	10.50
	700 °C	2.21	0.55	0.53	10.04	0.75	10.59
	750 °C	1.68	1.28	0.45	4.10	0.88	5.38
	800 °C	2.05	0.96	0.54	3.79	0.84	4.75
	850 °C	2.59	0.90	0.80	3.92	0.74	4.82

The error margins of the reported values range at Table 2 are between 3% and 10%.

$$C = (R^{1-a}Q)^{1/a} \quad (1)$$

In the initially observed R_2Q_2 circuit, as the a_1 values approach unity, the extracted capacitance values fall within the range of 10^{-7} – 10^{-6} F/cm², which is associated with typical double-layer capacitance behavior. Also, as evidenced in Figure 5c at 800–850 °C and Figure 5b at 850 °C, the corresponding Nyquist arcs tend to originate above the real axis on the imaginary axis [46,47].

As shown in Table 2, the R_{ASR} values decrease with increasing temperature for all samples, and the effect of cerium content on the polarization resistance is observable. The higher concentration of cerium in the structure increases the transfer of oxygen ions; therefore, C5 showed the lowest polarization resistance compared to the other electrocatalysts. However, at temperatures above 800 °C, an increase in capacitance and the appearance of double peaks are observed in symmetrical cells with a cerium content greater than 0.15, attributed to the formation of an interface at the electrode/electrolyte interface. In the desorption profile shown in Figure 4, the desorption peak intensity of C9 was the lowest, which was reflected in the high resistances observed in the impedance measurements. The issue may be related to structural changes induced by cerium addition, where a 10% increase negatively affects both oxygen and electronic mobility. The $\text{PrMnO}_{3-\delta}$ -based C9 electrode performed.

The total polarization resistance of the C5 catalyst supported on ScSZ electrolyte demonstrated comparable performance to that reported for $\text{Sr}_x\text{Ca}_{1-x}\text{Mn}_{1-y}\text{Si}_y\text{O}_{3-\delta}$ (12.3 and 11.07 $\Omega \cdot \text{cm}^2$ at 700 °C, Porras-Vazquez et al. [48]), Pr_2CuO_4 on CGO (3.7 $\Omega \cdot \text{cm}^2$ at 800 °C, $p\text{O}_2 = 1.8 \times 10^{-3}$ atm, Lyskov et al. [49]), and $(\text{Sr}_{1-x}\text{Pr}_x)_{0.95}\text{FeO}_{3-\delta}$ on LSGM (8.75 $\Omega \cdot \text{cm}^2$ at 700 °C, Sánchez-Caballero et al. [50]). Compared to the traditional LSM catalyst on the same ScSZ electrolyte, the C5 catalyst exhibited lower resistance values over a lower operating temperature range of 700–850 °C than the $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{MnO}_3$ cathode (sintered at 1300 °C) at 950 °C, as reported by Chen et al. [51], while exhibiting similar values with other synthesized LSM-based catalysts in the same study. Additionally, the C5 catalyst showed comparable performance to the LSM–GDC30 cathode on YSZ at 700 °C, as reported by Murray and Barnett [52].

The linearity of the electrode resistance versus reciprocal temperature was investigated using the Arrhenius equation, with individual arc resistances analyzed in the Nyquist plots, as well as the overall ASR values. The plots on the left in Figure 6 display an increase in E_a with decreasing temperature for R_3 in the lower-frequency region, indicating thermally activated charge-transfer behavior, while R_2 exhibits a nearly temperature-independent trend for most cells. The upper left plot in Figure 6 displays the derived activation energies for the C1, C9, C8, and C5 electrodes, respectively, at 99.6, 83.5, 46.4, and 34.8 kJ/mol, in

accordance with the literature [53–55]. The results indicate that C9 and C8 exhibit a higher E_a compared to C5 and C8.

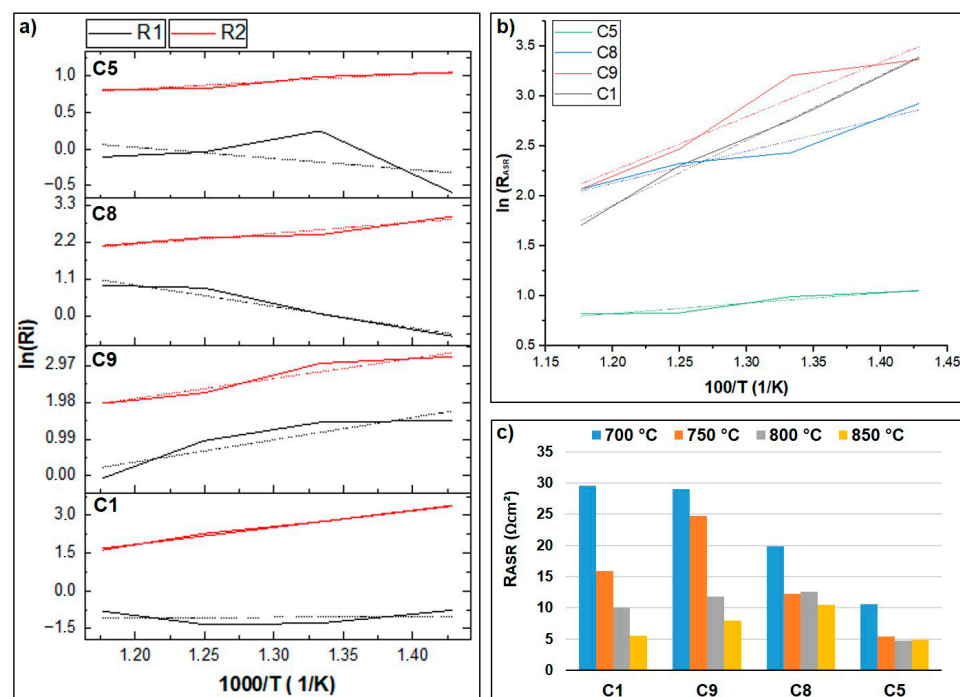


Figure 6. Comprehensive results of (a) Arrhenius calculation for the individual main resistances, (b) Arrhenius calculation of ASR resistances at 700 °C to 850 °C, and (c) ASR values of the electrocatalyst.

Figure 7 shows the Nyquist plot of PrCeMn-ScSZ and PrCeMn-YSZ symmetrical cells measured at 700 °C to 850 °C in an air environment. Impedance measurements were performed on cells with identical C5 electrode applied on both YSZ and ScSZ electrolytes. The polarization resistances for C5 on YSZ electrolyte were 19.12, 8.37, 6.61, and 6.17 $\Omega\cdot\text{cm}^2$ while on ScSZ electrolyte, they were 12.63, 7.07, 4.7, and 4.97 $\Omega\cdot\text{cm}^2$ at 700, 750, 800, and 850 °C, respectively.

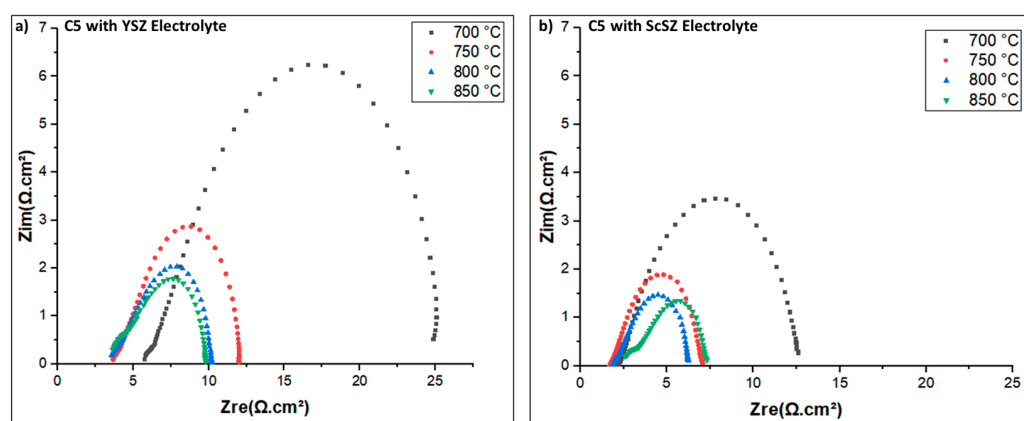


Figure 7. Impedance measurements from 700 °C to 850 °C for (a) C5-YSZ and (b) C5-ScSZ symmetrical cells.

As the temperature increases, both systems exhibit improved ionic conductivity and enhanced surface exchange kinetics for both electrolytes, resulting in a decrease in polarization resistance. The C5 electrocatalyst demonstrated better compatibility when used with a ScSZ electrolyte instead of YSZ. Using ScSZ electrolyte, the C5 electrocatalyst exhibits lower

resistance results, 28% lower compared to the YSZ used at a midpoint temperature of 800 °C for all cells. In the study by Huang et al., 2002, a polarization resistance of approximately $4\ \Omega\cdot\text{cm}^2$ was reported for a $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ electrode on YSZ with a similar electrolyte thickness [56]. In the present work, a comparable effect to that of strontium was achieved by cerium substitution when using a ScSZ electrolyte. The C5 catalyst on YSZ electrolyte exhibited a higher polarization resistance value compared to the $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{MnO}_3$ cathode (sintered at 1300 °C), which demonstrated a value below $15\ \Omega\cdot\text{cm}^2$ at 950 °C, as reported by Chen et al. [51].

3. Materials and Methods

3.1. Synthesis of the $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ Electrocatalysts

$\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ electrocatalysts were prepared by the sol–gel combustion method with a ratio of metal to glycine to citric acid of 1:1.5:1.5 in the starting solution [57]. In preparing the perovskite electrocatalyst, the metal ratios of the A-side (praseodymium and cerium) and B-side (manganese) are adjusted to 1:1, while the ratio of the A-side metals of Pr:Ce was maintained at 0.5:0.5, 0.85:0.15, 0.9:0.1, and 1:0 in the starting solution. The starting solution was prepared with high-purity metallic salts in water media with the specified concentrations of glycine and citric acid. The pH of the starting solution is then adjusted to 7 with a 1 M ammonia solution, and the gel is formed by evaporation at 80 °C. The final product is obtained after the formed gel was oven-dried at 250 °C and calcined at 1000 °C. In terms of convenient tracking, prepared $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ electrocatalysts were coded as C5 for the 0.5:0.5 Pr:Ce ratio, C8 for the 0.85:0.15 Pr:Ce ratio, C9 for the 0.9:0.1 Pr:Ce ratio, and C1 for the 1:0 Pr:Ce ratio.

3.2. Symmetrical Cell Fabrication

To evaluate the impedance electrocharacteristic behaviors of the prepared electrocatalysts as well as the YSZ and ScSZ electrolytes by EIS, symmetrical cells were prepared via electrolyte support with press method. In order to obtain homogenous powder, YSZ were ball milled at 100 rpm rotation speed for 24 h by wet milling. Prepared powders then were sieved through 100 micron. YSZ powders were transformed into pellets by applying 5 tons of pressure. Afterwards, the final shape of the 2 cm diameter, 1 mm thick pellets was achieved after heat treatment at 1450 °C for 3 h. Since the ScSZ powder exhibited a sufficiently fine particle size to readily pass through a 100 μm sieve, additional pre-treatment via ball milling was not implemented. ScSZ powders were pressed into pellets using the same procedure as for YSZ, and 2 cm diameter pellets with 1 mm thickness were obtained after heat treatment at 1400 °C for 3 h.

The synthesized $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ electrocatalyst was applied to both sides of the electrolyte pellets of YSZ and ScSZ using the spray coating method. The coating slurry was prepared by dispersing 30% alpha-terpineol and 70% powder (containing 95% catalyst and 5% ethyl cellulose) in isopropanol and homogenized by ball milling at 150 rpm for 1 h. The symmetrical cells were obtained by uniformly coating both sides of the electrolyte pellets with the prepared slurry, resulting in an active electrode area of 0.8 cm in diameter on each side. The coated pellets were calcined at 1100 °C for 4 h to remove organic binders to obtain the stable formation of an electrode–electrolyte interface.

3.3. Characterization Methods

X-Ray diffraction (XRD), were used for crystal structural evaluation of the synthesized electrocatalyst via Empyrean MultiCore diffractometer (Malvern Panalytical, Malvern, UK) using the $\text{CuK}\alpha$ radiation (K-Alpha; $1.54060\ \text{\AA}$) between 10 and 90°. The phase measurements were identified by reference to International Center for Diffraction Data

(ICDD). Phase transitions upon cerium addition and the formation of perovskite and secondary phases were evaluated via XRD to identify the structural changes of cerium addition to the PrMn structure.

X-Ray photoelectron spectroscopy (XPS) was used for the oxidation state of the cations and surface composition of electrocatalyst via X-ray Photoelectron Spectroscopy (XPS) with a K-Alpha instrument (Thermo Fisher Scientific Inc., Waltham, MA, USA), and data were analyzed using the curve fitting application. All measurements were conducted at ambient temperature under a high-vacuum environment (PO_2 between 10^{-8} to 10^{-9} mbar) in the analysis chamber. The technique provides insights into the compositional state of the electrolyte as well as the oxidational states of the elements and state of oxygen lattice.

Oxygen temperature-programmed desorption (O_2 -TPD) analyses were conducted to help in the understanding of the $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ catalysts' oxygen diffusion characteristics and surface oxygen mobility. TPD reactions were carried out on a tubular reactor system that was presented in previous works [58], with continuous flow in an oxygen atmosphere, and analysis were performed by mass spectrometry (Hiden Analytical QGA Quadrupole Mass Spectrometer, Warrington, UK). Approximately 100 mg of the catalyst was loaded on quartz wool in the heated core of the tubular reactor and was pretreated in an argon-balanced 10% oxygen environment (total flow: 40 mL/min), which heated to 750 °C and cooled to room temperature in a controlled manner. When sample reached room temperature, the flow was switched to argon (40 mL/min) and after stabilization in the mass spectrometer, the temperature was increased to 900 °C at 3 °C/min [59].

Hydrogen temperature-programmed reduction (H_2 -TPR) was conducted for evaluation of reduction behavior of electrocatalysts at hydrogen atmosphere by using a mass spectrometer. TPR studies were carried out on 5% H_2 -balanced N_2 with 3 °C/min heating ramp from room temperature to 1000 °C on a tubular reactor with continuous flow. The outer gas samples were directed to the mass spectrometer and analyzed via mass spectrometer.

Electrochemical impedance spectroscopy: Impedance measurements of symmetrical cells were analyzed at different temperatures using a ProboStatTM system (NorECs, Oslo, Norway), and the data were collected using a VersaSTAT4 potentiostat-galvanostat (Princeton Applied Research, Ametek Scientific Instruments, Oak Ridge, TN, USA). Impedance measurements of $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ electrocatalyst-coated symmetrical cells were carried out in dry air at temperatures between 700 and 850 °C over a frequency range of 100,000–0.001 Hz with an AC amplitude of 40 mV.

4. Conclusions

Novel $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ electrocatalysts were successfully synthesized via the sol–gel combustion method with different Pr:Ce ratios of 1:0, 0.9:0.1, 0.85:0.15, and 0.5:0.5 to evaluate their characteristics and electrochemical properties for SOFC electrode material. The prepared electrocatalysts were calcined at 1000 °C before characterization experiments to obtain a final structure with minimal impurities. Structural properties were analyzed using X-Ray diffraction (XRD), which revealed that the addition of cerium to the praseodymium manganese structure induced phase transitions and structural changes, resulting in the formation of $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ phases. The presence of surface oxidation states is observed for cerium in the +4 state, praseodymium in the +3 state, and manganese primarily in the +3 state, as determined by X-Ray photoelectron spectroscopy (XPS) analysis, which is essential for understanding the electrocatalytic behavior.

For oxygen characteristic results of O1s orbitals, XPS analysis and temperature-programmed desorption (TPD) indicated that the O1s orbitals for all electrocatalysts exhibited a characteristic O_β peak at a binding energy of around 530 eV, which is associated with lattice oxygen. The peak intensities corresponding to oxygen vacancy properties were

the lowest for C9, as indicated by the higher resistance characteristics in the impedance results. In contrast, the C5 catalyst, with a higher intensity, showed lower resistances due to enhanced oxygen mobility and more efficient oxygen exchange at the catalyst surface. The characteristic results not only validate the role of cerium as an ionic conductor in studies but also demonstrate an improvement in catalytic performance when using the same proportion of Pr and Ce in $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ electrocatalysts.

Impedance spectroscopy (EIS) measurements were used for electrochemical resistance analysis for $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ catalysts at intermediate temperatures from 700 to 850 °C. $\text{Pr}_{0.5}\text{Ce}_{0.5}\text{MnO}_{3-\delta}$ catalyst (C5) exhibited the lowest polarization resistance at 700 and 750 °C, making it the most efficient electrocatalyst among those tested for lower temperatures. However, as the temperature increases, the addition of cerium causes structural distortions that lead to increased capacitance at higher temperatures. At 800 and 850 °C, the $\text{PrMnO}_{3-\delta}$ (C1) electrocatalyst showed promising performance with low resistance and high structural stability. According to this study, the optimal Pr:Ce ratio was 50:50 (C5), which resulted in improved performance with reduced resistance and increased catalytic activity. The recognition of cerium's presence as a crucial element in enhancing the electrochemical performance of $\text{Pr}_x\text{Ce}_{1-x}\text{MnO}_{3-\delta}$ electrocatalysts led to improved oxygen ion transfer.

The electrocharacteristic study of C5 catalyst on YSZ and ScSZ electrolytes in solid oxide fuel cells (SOFCs) provides valuable insights into the cell performance of the prepared electrocatalyst. The experimental results indicate that C5 electrode used on ScSZ electrolyte shows a lower polarization resistance of up to 28% at 800 °C compared to YSZ, which is widely used for its high ionic conductivity at elevated temperatures. Moreover, with the ScSZ electrolyte, C5 exhibited lower polarization resistance and demonstrated the ability to operate at lower temperatures compared to YSZ.

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