Correlations between Oxygen Uptake and Vacancy Concentration in Pr-Doped CeO₂
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ABSTRACT: The oxygen uptake of a series of Pr–CeO₂ materials was measured using thermogravimetric analysis at 420 and 600 °C, and at both temperatures, 20% Pr–CeO₂ was found to have the highest uptake. The materials were characterized using X-ray diffraction and scanning transmission electron microscopy. Defects in the materials were identified using Raman spectroscopy, and ultraviolet-visible spectroscopy was used to show the presence of Pr cations in the +3 oxidation state. The existence of these species was attributed to be responsible for the ability of the materials to uptake oxygen. Electron energy loss spectroscopy was used to investigate the effect of Pr addition to CeO₂; the Ce M₅/M₄ and O K₂/L₂ ratios were calculated to indicate the relative changes in the Ce³⁺ and oxygen vacancy concentration, respectively. There was no observable increase in the Ce³⁺ concentration; however, the oxygen vacancy concentration increased with an increase in the Pr content. Thus, Pr increases the defect concentration and the ability of the materials to uptake oxygen.

INTRODUCTION
From both an environmental and industrial perspective, the need to develop low-cost oxygen generation technologies is ever-increasing. High-purity (>99%) oxygen is currently generated cryogenically, which requires high energy consumptions, typically of ∼200–220 kW h per tonne of O₂ produced.¹ The energy associated with the air separation unit (ASU) of the plants contributes to the increasing “carbon debt” of the world. Approximately 35% of greenhouse gas emissions arise from energy supply because of the combination of large energy penalties in production and low efficiencies for conversion, transmission, and distribution.² Although research has focused on reducing the energy and the associated cost of ASU through the modification of existing systems, sorbent- and membrane-based alternatives have also been proposed as methods of energy reduction.

Applications of CeO₂-based materials as solid oxide fuel cells, catalysts, oxygen sensors, and oxygen separation membranes are driven by the requirements for materials to exhibit both high and reversible oxygen storage capacities (OSC), good electronic and ionic conductivity, and chemical stability and consist of relatively inexpensive components. CeO₂ can reversibly uptake oxygen because of a change in the Ce valence state under reducible conditions. Under low partial pressure of oxygen (pO₂) conditions, Ce⁴⁺ cations are reduced and oxygen is removed from the crystal lattice. Conversely, by increasing pO₂, oxygen migrates into the lattice and Ce³⁺ cations are oxidized. When +3 cations are present, ionic conductivity arises as oxygen ions move toward oxygen vacancies, and electronic conductivity arises from the electron movement by a polaron hopping mechanism.³ Polaron hopping exhibits a temperature-dependence, in which at higher temperatures electrons are able to move by hopping from Ce³⁺ to Ce⁴⁺.⁴ In the work by Su et al.,⁵ charge transfer on a CeO₂(111) surface with defects was found to occur by polaron migration followed by oxygen diffusion.

The rare-earth cations, Tb and Pr, have been used as dopants to enhance the redux properties of CeO₂. Higher oxygen uptakes are achieved via the formation of extrinsic lattice defects or intrinsically through the removal of oxygen anions from thermal treatment/reduction.⁶ The multivalent (+3/+4) nature of Pr and Tb can further enhance the vacancy concentration of CeO₂ and increase both the electronic and ionic conductivities.⁷ The increased oxygen uptake of Pr–CeO₂-based materials can be attributed to the variable valence nature and high reducibility of Pr; under a flow of He, Pr⁴⁺ can be reduced, whereas Ce⁴⁺ requires a reducing gas such as H₂. During reduction, oxygen is removed from the lattice, generating vacancies and +3 cations that are required to maintain the charge balance of the lattice.⁸ At 700 °C, pO₂ of >10⁻⁷ atm was found to be required for the oxidation of Pr³⁺ in Ce₀.₈Pr₀.₂O₂–δ.⁹ The pO₂ required for the oxidation of Ce³⁺ to Ce⁴⁺ at room temperature is 10⁻³⁰ atm.¹⁰ High reducibility of the Pr-based materials can also be achieved at temperatures <250 °C.¹¹ The lower reduction temperature can be attributed to the lower cation reduction energy; 1.83 eV was required to
reduce two Pt$^{4+}$ cations, however, 4.38 eV was needed for the reduction of two Ce$^{4+}$ cations.\textsuperscript{12} With the addition of Pr, the reduction energy of CeO$_2$ decreases twice that of the Pr ionization energy.\textsuperscript{13,14} The nonstoichiometry of Pr$-$Ce oxides varies the reduction enthalpy,\textsuperscript{15} and for Ce$_{0.8}$Pr$_{0.2}$O$_2$ $\delta$ it has been reported to be 2.9 $\pm$ 0.3 eV via Coulometric titration.\textsuperscript{16} Chatzichristodoulou and Hendriksen\textsuperscript{17} found that the oxygen nonstoichiometry of Ce$_{0.8}$Pr$_{0.2}$O$_2$ could be modeled using an excess enthalpic term ($\Delta H_{\text{exc}}$) linear in $\delta$ (oxygen nonstoichiometry) and defects could be randomly distributed through the lattice. In their work, the reduction behavior of Pr could be described using a 6-linear (nonideal) defect model by estimating the oxidation partial molar enthalpy and entropy. Overall, Pr$-$CeO$_2$-mixed oxides have a lower reduction temperature than pure CeO$_2$ and have a greater oxygen storage and release capacity.\textsuperscript{18} Thus, Pr$-$CeO$_2$-mixed oxides have been proposed to have applications as oxygen separation materials.

Electron energy loss spectroscopy (EELS) allows for nanometer-length-scale resolution and has been used for the investigation of Pr$-$CeO$_2$ materials. Niu et al.\textsuperscript{19} reported a decrease in the antibonding Ce peak intensity from the introduction of Pr, evidencing an increase in the Ce$^{3+}$ fraction and an increase in the Ce $I_{M4}/I_{M4}$ ratio with increased % Pr. In their work, the Ce $I_{M4}/I_{M4}$ ratio of CeO$_2$ was 0.78, 10% Pr$-$CeO$_2$ was 0.82, and 60% Pr$-$CeO$_2$ was 1.17. Scanning transmission electron microscopy (STEM$-$EELS) was used by Rodríguez-Luque et al.\textsuperscript{20} to demonstrate the segregation of Pr cations on the surface of CeO$_2$ particles. Investigations were focused on the Ce edge because of the reducible nature of Pr, which showed the Ce oxidation state varied throughout the particle and that Ce$^{3+}$ was primarily located on the surface. In situ transition electron microscopy (TEM) studies of the reduction process of Rh/Ce$_{0.8}$Pr$_{0.2}$O$_2$ catalysts heated under H$_2$ to 950 °C show that the Ce and Pr edges undergo a 1.4 eV shift to lower energy, the Ce antibonding peak intensities decrease and, for the Pr edge, a peak appears on the lower energy side of the M$_4$ peak.\textsuperscript{21} Furthermore, evidence of oxygen vacancy ordering was first observed at 700 °C, although the reduction of Pr$^{4+}$ occurs below this temperature. The segregation of Gd in CeO$_2$-based electrolytes has also been evidenced from the integrated intensity ratio of the Gd N$_{5.4}$ and Ce N$_{5.4}$ edges and increased Pr, Gd, and Ce$^{3+}$ concentrations from the respective Pr M$_{5.4}$, Gd M$_{5.4}$, and Ce M$_{5.4}$ edges.\textsuperscript{22} Ultrahigh-energy-resolution valence-loss EELS has been used by Bowman et al.\textsuperscript{23} to measure the band gap states in Pr$_{1-x}$Ce$_x$O$_2$.

In a similar Tb$-$CeO$_2$ system, we have recently reported the qualitative trends between the Ce$^{3+}$ and the oxygen vacancy concentration, % Tb, and oxygen uptake for a series of Tb$-$CeO$_2$ materials.\textsuperscript{24} This work showed that by increasing the % Tb the oxygen vacancy concentration and the oxygen uptake increased. However, it was also found that there was no observable change in the Ce$^{3+}$ concentration. Here, we have extended this work to report the effect of % Pr on the oxygen uptake, Ce$^{3+}$, and the oxygen vacancy concentration of CeO$_2$. To our knowledge, this is the first fundamental study identifying and detailing the correlations between the Pr defect (oxygen vacancy), and Ce$^{3+}$ concentrations with oxygen uptake. Oxygen uptakes were determined in gas-switching experiments using thermogravimetric analysis (TGA). The materials were characterized using X-ray diffraction (XRD) and STEM. Diffuse reflectance ultraviolet-visible (DR UV-Vis) spectroscopy was used to determine the presence of Pr$^{3+}$

## EXPERIMENTAL SECTION

### Material Preparation

The Pr$-$CeO$_2$-mixed oxides (Pr = 10, 15, and 20 mol %) were prepared by coprecipitation from (NH$_4$)$_2$Ce(NO$_3$)$_6$ (Aldrich, >98.5%), Pr(NO$_3$)$_3$-6H$_2$O (Aldrich, 99.9%), and urea (15× the total ion concentration, Sigma-Aldrich, 99–100.5%), which were dissolved in water and heated at 90 °C for 8 h. Pr$_{2-x}$O$_x$ was prepared using the same conditions with Pr(NO$_3$)$_3$-6H$_2$O (Aldrich, 99.9%) and urea. The resultant precipitates were filtered, washed with water and ethanol, and dried overnight in an oven at 100 °C. The materials were heated under a nitrogen atmosphere to 700 °C for 2 h with a heating rate of 2 °C min$^{-1}$.

### X-Ray Diffraction

XRD patterns were collected on a Bruker D8 Focus diffractometer equipped with a monochromatic Cu K$\alpha$ ($\lambda = 1.5406$ Å) source operated at 40 kV and 40 mA. The data were collected over a 2θ range of 5–80, with a step size of 0.02° and a step time of 1° min$^{-1}$.

### Thermogravimetric Analysis

To quantify oxygen uptake, gas-switching experiments were carried out using a Mettler Toledo TGA/DSC 1 system. The samples were weighed (∼10 mg) into an alumina crucible (150 μL) and heated to 420 and 600 °C in a flow of nitrogen (35 mL min$^{-1}$) before instrument air was introduced (35 mL min$^{-1}$), after which nitrogen was then reintroduced. The flow of air was mixed with a N$_2$ carrier gas that resulted in a pO$_2$ of 13.3 kPa delivered to the sample. When the gas was switched to instrument air the weight increase was used to calculate the oxygen uptake. To ensure data consistency, averages were obtained from a minimum of two separate experiments with a maximum of three standard errors of the mean.

### Raman Spectroscopy

The spectra were obtained using a Renishaw inVia Raman spectrophotograph with an excitation wavelength of 632.8 nm from a HeNe source. The spectra were obtained between 200 and 200 nm, with a spot size of ~1 μm and a laser power of 1 mW on the sample.

### DR UV–Vis Spectroscopy

The presence of Pr$^{3+}$ was identified using a Cary 5000 spectrometer fitted with a DR accessory. The spectra were obtained with a 1 nm data interval between 800 and 200 nm in % reflectance mode with polytetrafluoroethylene as the reference followed by applying the Kubelka–Munk equation.

### Transmission Electron Microscopy

STEM bright-field (BF) and high-angle annular dark-field (HAADF) images were obtained at 200 kV on an FEI Tecnai G2 F20 S-TWIN FEGTEM instrument. All samples were prepared by dispersing into butanol and ultrasonicating before dipping an ultrathin holey carbon film into the solution.

EELS measurements were recorded using a JEOL JEM-2100F FEGTEM and Gatan 776 Enfina 1000 parallel detection EELS spectrometer by the method described in D’Angelo et al.\textsuperscript{24} The spectra were obtained in diffraction mode using a condenser aperture of 40 μm, a spot size of 1 μm, a dispersion of 0.1 eV/channel, and a collection aperture of 3 mm. Approximately 10 spectra were acquired from different clusters located on the grid with individual crystallites in random orientation. The data were obtained using an acquisition time of 5 s and by summing 20 spectra. These conditions allowed for
beam damage to be minimized and compositional variations and orientation dependence variation to be eliminated. The background was subtracted using the power-law technique, and the integrated white-line intensities were determined using a 16 eV window for Ce M\textsubscript{5,4} and a 2 eV window for the O I\textsubscript{p}/I\textsubscript{c} edge.

■ RESULTS AND DISCUSSION

Structural and Morphology Characterization. The diffraction patterns of the Pr−CeO\textsubscript{2} materials are presented in Figure 1 and show that all reflections can be indexed to the cubic fluorite structure (space group Fm\textsubscript{3}m) of CeO\textsubscript{2} (JCPDS card 00-034-0394). Pr−CeO\textsubscript{2}-mixed oxides with >20% Pr exhibited phase segregation, as shown in Figure S1; hence, these were not used further in this study.

STEM BF and HAADF images (Figure 2a−c) showed that the materials comprised aggregated crystallites ∼10 nm. A d-spacing of 0.31 nm can be seen for 20% Pr−CeO\textsubscript{2} in Figure 2c, which corresponds to the (111) plane of the CeO\textsubscript{2} cubic fluorite lattice. The images of the synthesized pure PrO\textsubscript{2−δ} show that the particles were aggregated and had an elongated octahedral-type morphology (Figure 2d). Further images of the materials are presented in Figure S2.

Measurement of Oxygen Uptake Using TGA. The oxygen uptake of Pr−CeO\textsubscript{2} was measured in gas-switching experiments using TGA, and the results are shown in Figure 3. The oxygen uptake increased by increasing the % Pr and the analysis temperature. At 420 °C, the uptakes for Pr = 10, 15, and 20% were 24, 31, and 41 μmol·g\textsuperscript{−1}, respectively. In this work, the temperature (420 °C) required for the uptake was comparable with the temperatures used by Mullhaupt\textsuperscript{29} for Ce−Pr materials (380−606 °C). Oxygen uptake is considered to be primarily due to the reduction of Pr, in contrast to the reduction of Ce. This is because lower pO\textsubscript{2} (<10−30 atm at room temperature) and higher temperatures (>2000 K at ambient pressure) are required to remove oxygen from CeO\textsubscript{2}.\textsuperscript{10} Oxygen desorption from PrO\textsubscript{2} thin films occurs over the range 377−517 °C as a result of a PrO\textsubscript{2} → Pr\textsubscript{5}O\textsubscript{9} transition.\textsuperscript{30} Similarly, the temperature-programmed reduction of PrO\textsubscript{11} under H\textsubscript{2} showed a main peak at 517 °C, assigned to the maximum amount of bulk oxygen loss. Oxygen vacancies are generated in the crystal structure from the addition of Pr, which increases the ability of the materials to lose oxygen.

Increasing the analysis temperature from 420 to 600 °C resulted in overall increase in the uptake at each % Pr. The uptakes when Pr = 10, 15, and 20% were 33, 55, and 95 μmol·g\textsuperscript{−1}, respectively. These values are significantly higher than the measured uptake of <5 μmol·g\textsuperscript{−1} for CeO\textsubscript{2}.\textsuperscript{8} However, it is considered that weight loss due to the removal of water vapor also contributes to the measured weight loss. Overall, Pr was found to promote the oxygen uptake of CeO\textsubscript{2} at both 420 and 600 °C.

Analysis of Defects Using Raman and DR UV−Vis Spectroscopy. The presence of defects in the Pr-doped CeO\textsubscript{2} materials was determined through Raman spectroscopy and DR UV−vis spectroscopy. A 633 nm Raman excitation laser was
selected to increase the laser penetration depth and provide bulk and surface information by minimizing optical absorption. Figure 4a shows the presence of an $F_{2g}$ band at 460 cm$^{-1}$ due to a CeO$_8$-type complex with $O_h$ symmetry and a wide defect band at 500−650 cm$^{-1}$. As suggested by Li et al.,32 because of the similar ionic radii of the +3 and +4 Ce and Pr cations, the presence of this defect band is likely from the differences in oxidation states rather than differences in ionic radii. The defect band has been reported to consist of two modes at 560 and 584 cm$^{-1}$ from metal−O complexes both with and without vacancies.33 Through peak-fitting of the Pr = 20% material spectra using a Lorentzian function, these two species are suggested to be present in the synthesized Pr-doped CeO$_2$ materials. Defects are introduced into the crystal structure when Pr is added to CeO$_2$ as this defect mode is not present for CeO$_2$. For every two +3 cations, one oxygen vacancy is needed to maintain the charge balance of the lattice.

It can also be observed that the $F_{2g}$ band exhibits a downward shift with increasing % Pr. A shift in the $F_{2g}$ mode of the rare-earth-oxide-doped CeO$_2$ materials has been attributed to the lattice contraction and/or the introduction of vacancies.34 Lattice contraction may occur by increasing the % Pr as Pr$^{4+}$ (Pr$^{4+}$ = 0.96 Å) cations are smaller (but only slightly) than those of Ce (Ce$^{4+}$ = 0.97 Å).35 Lee et al.36 attributed the downward shift in the $F_{2g}$ band of CeO$_2$ nanorods to volume expansion from the generation of vacancies; the larger the shift, the higher the expected oxygen vacancy concentration. It is predicted that when Pr cations are incorporated into the CeO$_2$ lattice there is a mixture of Pr in both the +3 and +4 oxidation states. These findings correspond to the understanding that pure PrO$_{2−δ}$ possesses cations in both the +3 and +4 oxidation states.37 As the amount of added Pr increases, the concentration of cations in both the +4 and +3 oxidation states is considered to increase. Although vacancies are present in these materials as shown by the defect band at ~500−650 cm$^{-1}$, if the concentration of these cations is low, then the lattice may still contract from the increasing amount of Pr$^{4+}$ and result in the $F_{2g}$ mode shift. Ahn et al.12 reported for a series of Pr-doped CeO$_2$ using density functional theory (DFT) calculations, that Pr$^{3+}$ was present as the majority ion and Pr$^{4+}$ as the minority ion. The concentration of vacancies and +3 cations is likely not great enough to result in an observable expansion of the lattice cell.

DR UV−vis spectra of CeO$_2$ and the Pr−CeO$_2$ materials are presented in Figure 4b. In all spectra, the peak present at ~250 nm corresponds to Ce$^{3+}$ from a O$_2^−$→Ce$^{3+}$ charge transfer, the peak at ~280 nm corresponds to a O$_2^−$→Ce$^{4+}$ charge transfer, and the peak at ~330 nm corresponds to an interband transition from the O 2p to Ce 4f band.38 In addition, a strong absorption is observed between 400 and 650 nm for the Pr−CeO$_2$ materials because of Pr$^{3+}$ transitions. In the work by Kasprowicz et al.39 on Pr-doped Bi$_2$ZnOB$_2$O$_6$, Pr$^{3+}$ absorption bands between 430 and 490 nm were attributed to $^3H_4$ ground state to $^3P_4$ transitions and those between 560 and 610 nm from $^3H_4$ to $^1D_2$ transitions. Also, in the work by Strze$\tilde{p}$ et al.,40 a prominent 488 nm 4f−4f band was assigned to $^3H_4$ transitions to $^3P_4$ multiplets. It has been reported that Pr$^{4+}$ does not absorb in the UV−vis region.41,42 Overall, our results show that the Pr−CeO$_2$ materials contain Pr cations in the +3 oxidation state and oxygen defects/vacancies.

**Figure 4.** (a) Raman spectra of CeO$_2$ and Pr−CeO$_2$ with Pr = 10, 15, and 20% showing the defect band characteristic of vacancies. (b) DR UV−vis spectra of CeO$_2$ and Pr−CeO$_2$ with Pr = 10, 15, and 20%.

**Figure 5.** (a) Ce M$_{4,4}$ white lines of CeO$_2$ and Pr−CeO$_2$ with % Pr = 10, 15, and 20 and (b) M$_4$ and M$_4$ white lines of PrO$_{2−δ}$.
investigate the relative changes in Ce$^{3+}$ and oxygen concentration of the Pr–CeO$_2$ materials. The background-subtracted Ce M$_{4,5}$ EELS spectra of CeO$_2$ and the Pr–CeO$_2$ materials are presented in Figure 5a and show the presence of two Ce white lines at 883 and 901 eV due to 3d$_{5/2}$ → 4f$_{7/2}$ (M$_5$) and 3d$_{3/2}$ → 4f$_{5/2}$ (M$_4$) electron transitions, respectively. When Pr is introduced, two Pr M$_{4,5}$ white lines can be observed at 951 and 931 eV that are from 3d to 4f transitions and are characteristic of all lanthanides. The intensity of these peaks increases as the Pr content increases. On the higher energy side of the M$_{5}$/M$_{4}$ lines can be observed for PrO$_2$ $\sim$ 1/3 of CeO$_2$, which results from both structural and electronic modiﬁcations. $\delta$ is a function of Ce cations in Pr–CeO$_2$ solid solutions does not vary from that of the initial CeO$_2$ (+4). Furthermore, there is no observable decrease in the Ce and Pr satellite peak intensity as the amount of % Pr increases. Consequently, we interpret the Ce +4/+3 concentration to not vary or at least not signiﬁcantly or detectably using this method. At higher % Pr, the intensity of the antibonding transitions has been found to decrease for Ce$_{0.9}$Pr$_{0.1}$O$_2$ thin ﬁlms on Si(111) as the amount of Ce$^{3+}$ in the materials increases. As there is no variation in the Ce ratios of the synthesized and Pr–CeO$_2$ materials or in the intensity of the Ce satellite peaks, the increase in the spectral changes are considered to be due to the introduction of Pr.

The O K (1s) near-edge ﬁne structure spectra of the Pr–CeO$_2$ materials are presented in Figure 7. The CeO$_2$ ground state has a ﬁlled oxygen 2p valence band and, because of the strong hybridization between Ce levels and O 2p orbitals, the electronic structure has been reported to be a mixture of 4f$^0$ and 4f$^2$–O 2p states. Because of dipole selection rules, only an s → p transition is permitted; however, this mixing allows for electric dipole transitions from the O 1s orbital to the p-like component of the Ce 4f and 5d states. Similarly, when Pr is added, the mixing of O 2p and Pr 4f states also allows for these transitions. The peak labeled “A” arises from O 1s → Ce 4f transitions, and peaks “B” and “C” arise from O 1s → Ce 5d→eg and 5d→t$_{2g}$ levels in the conduction band, respectively. An increase in the ratio between the peaks labeled B and C has been reported as indicative of the presence of vacancies or defect sites within the crystal lattice. The O I$_{g}$/I$_{c}$ ratio for CeO$_2$ was 0.68 and that for Pr = 10, 15, and 20% was 0.70, 0.74, and 0.76, respectively. The higher O I$_{g}$/I$_{c}$ ratio for the Pr–CeO$_2$ materials, compared to CeO$_2$, shows that the vacancies are generated by the addition of Pr. The vacancies that are generated have been reported to primarily exist around Pr ions rather than Ce. Pr–CeO$_2$ has a vacancy formation energy of $\sim$1/3 of CeO$_2$, which results from both structural and electronic modiﬁcations of the lattice. Also, our results reveal that the O I$_{g}$/I$_{c}$ ratio gradually increases with increasing % Pr. This increase was attributed to an increase in the vacancy concentration, which is likely responsible for the observed trend in oxygen uptakes as the % Pr increases.
Visual inspection of the O K (1s) fine structure shows that the peaks of the 20% Pr–CeO2 are slightly less defined and broader in comparison to those of CeO2. In ZnO nanocrystals, Zn L3 broadening and a weakened fine structure have been reported to be due to an increase in the vacancy concentration.\(^5\) Furthermore, the intensity of the peak labeled A appears to decrease relative to the peak labeled B with increasing % Pr. A decrease in the O I\(_g\)/I\(_c\) ratio for the Pr–CeO2 materials compared to CeO2 may be attributed to an increase in +3 cations filling the 4f state and inhibiting transitions. For CeO2-based materials consisting of only +3 cations, this peak is not present as the 4f orbital is occupied (4f\(^3\)).\(^48\) The structure can also be modified to result in the degradation of O 2p–Ce 4f hybridization and a decrease in the intensity of A.\(^5\)\(^4\)\(^5\) Distortion of the crystal lattice occurs as the introduction of Pr\(^{3+}/\)Pr\(^{4+}\) cations weakens the metal–oxygen bonds, lowering the reduction temperature and ease at which oxygen can be removed. The local structure near the vacancy is distorted as the lattice accommodates the larger Pr\(^{3+}\) cations that are generated during reduction.\(^1\) As the material is reduced and +3 cations/vacancies are generated, the resulting structural distortions can result in the broadening of the observed peak.\(^2\)\(^5\) An increase in vacancies and broadened O-extended fine structure have also been observed for vacancy concentrations of ∼4%.\(^5\)\(^6\)

The results presented here support those obtained using Raman spectroscopy that show the structure is modified through the addition of Pr from the presence of oxygen vacancy defects. The introduction of vacancies is also likely responsible for the exhibited oxygen uptake, where the higher the vacancy concentration, the higher the oxygen uptake.

**CONCLUSIONS**

In this work, the presence of vacancy defects in a series of Pr–CeO2-mixed oxides was determined to provide further insight into the oxygen uptake ability of CeO2-based materials. Correlations between the quantities of Pr added and the oxygen uptake, Ce\(^{3+}\) and oxygen vacancy concentration of CeO2 were established. The materials were synthesized with Pr = 10, 15, and 20%, and the oxygen uptakes were determined as a function of % Pr and at 420 and 600 °C. The highest uptake of 95 μmol·g\(^{-1}\) was achieved for 20% Pr at 600 °C and is higher than <5 μmol·g\(^{-1}\) obtained for CeO2. By increasing the analysis temperature, a greater portion of cations undergoes reduction to the +3 oxidation state, which, in turn, generates oxygen vacancies. The higher portion of defects acts as oxygen absorption sites to result in the increase in oxygen uptake with an increase in temperature and % Pr.

Vacancies were evident in the materials after the addition of Pr through Raman spectroscopy, as a broad defect band at 500–650 cm\(^{-1}\) was attributed to the combination of two modes because of oxygen vacancy defects and MO\(_3\) complexes containing a Pr cation without vacancy. A downward shift in the F\(_{2g}\) mode was also attributed to the increasing quantity of oxygen vacancies, and DR UV–vis spectroscopy showed the presence of Pr\(^{4+}\). To maintain the charge balance of the lattice, cations in the +3 oxidation state are required to accompany the oxygen vacancies.

EELS was used to qualitatively investigate the relative changes in Ce\(^{3+}\) and oxygen concentration through the calculation of the Ce I\(_{M1}/I_{M4}\) and O I\(_g\)/I\(_c\) ratios, respectively. The spectra of pure PrO\(_2\)–Pr show both smaller peaks on the high-energy side because of Pr\(^{4+}\) and a shoulder peak on the lower energy side of M\(_4\) from Pr\(^{3+}\), implying the oxide has mixed valence. By increasing the Pr content, there was no observable increase in the Ce\(^{3+}\) concentration. The oxygen vacancy concentration was found to increase when Pr was added to CeO\(_2\), which further increased with increasing Pr content. Thus, it was concluded that the observed oxygen uptakes of Pr–CeO\(_2\) were due to the presence of oxygen vacancies from the addition of Pr. These results emphasize the defect nature of Pr–CeO\(_2\) and may be used to develop materials requiring high oxygen uptakes.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00550.

XRD pattern of the Pr–CeO\(_2\) material with 30% Pr, STEM images of the Pr–CeO\(_2\)-mixed oxides and TEM image of PrO\(_2–\)Ce\(_2O_3\) TGA profile of PrO\(_2–\)Ce\(_2O_3\) and average EELS intensity ratios for CeO\(_2\) and Pr–CeO\(_2\) (PDF)

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Notes

The authors declare no competing financial interest.

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