Journal of Materials Chemistry A

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Journal:	*Journal of Materials Chemistry A*
Manuscript ID	TA-ART-05-2020-005137
Article Type:	Paper
Date Submitted by the Author:	19-May-2020

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ARTICLE

Understanding of A-site Deficiency in Layered Perovskites: Promotion of Dual Reaction Kinetics for Water Oxidation and Oxygen Reduction in Protonic Ceramic Electrochemical Cells

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Protonic ceramic electrochemical cells (PCECs) are a promising solid-state energy conversion device which enables conversion of energy between electricity and hydrogen at intermediate temperatures. Rapid conversion between chemical and electrical energy via PCEC technology will assist in meeting the energy storage grand challenge. To achieve highly efficient reversible operation between hydrogen production and electricity generation, boosting water-oxidation and oxygen reduction activities of the oxygen electrode while maintaining the durable operation is one of the early-stage technical opportunities. In this study, an A-site deficient layered perovskite $(PrBa_{0.8}Ca_{0.2})_{0.95}Co_2O_{6-\delta}$ has been developed as an oxygen electrode in a PCEC which presents superior electrochemical performances. The electrolysis current density has reached as high as -0.72 A cm^{-2} at 1.3 V , and the peak power density of 0.540 W cm^{-2} is obtained at 600 °C in electrolysis and fuel cell mode, respectively. The PCEC with the new electrode shows good durability against practical operation conditions for 160 hours in both operating modes with no observable degradation. The reversibility between electrolysis and fuel cell mode is also successfully demonstrated.

Introduction

As the renewable energy harvest becoming more accessible, the intermittency and fluctuation of the time and site-specific wind and solar energies can restrain the electricity supply into the grid.[1] Storing the energy for peak shaving can be a feasible approach to convert excessive electricity into chemical fuels that can be reversed to release the chemical energy.[2-4] Hydrogen is an energy dense carrier which has been widely used for various applications such as fuel cells and chemical industry.[5-6] To efficiently store electrical energy, solid oxide cells (SOCs) have been developed to convert energy between electricity and hydrogen fuel, which presents several advantages over other approaches such as low-temperature fuel cell and electrolyzers.[7-9] In the past decade, there has been significant progress in material development, electrochemical measurement, stability improvement, and stack-level study. However, wide-spread adoption of this technology has not been achived, due in part to the high operating temperatures (700~1000 °C) required by conventional oxygen-ion conducting electrolytes.[10-13] For example, yttrium-stabilized-zirconia still pose a series of problems such as material incompatibility between compartments, relative high temperature, fast degradation and expensive interconnects used in stacks.[14-15] In addition, nickel particle coarsening, and oxygen bubble generation are also identified as degradation mechanisms which contribute to electrode deterioration in electrolysis operation.[16-17]

Protonic ceramic electrochemical cells (PCECs) are an emerging technology that produces hydrogen and generates electricity within one single device at reduced temperature range (400~600 °C), in which the solid-state electrolyte has high proton conductivity due to lower activation energy for proton conduction.[18-22] Firstly, comparing with the conventional high-temperature SOCs, the intermediate temperature operation can greatly reduce the manufacturing cost as stainless steel may be utilized as interconnects and can also significantly improve the long-term operation stability.[23-24] Secondly, the dry hydrogen can be generated in the nickel-electrode side which avoids the further gas separation process while the nickel oxidation is also mitigated in fuel cell mode.[25-26] In addition, the delamination of oxygen-electrode/electrolyte interface due to high current density can be eliminated because the oxygen evolution reaction occurs on the entire electrode surface but not the electrode/electrolyte interface particularly when a mixed proton and electron conducting electrode is utilized.[27] In the past few years, there have been progressive development on material selection and improvements on electrochemical performance of PCECs, which demonstrates the fast hydrogen production and high power density at reduced temperatures.[28] However, some critical challenges still remain on material activity and stability, one of which is the electrode activity at intermediate temperatures when the current electrode materials particularly the oxygen electrodes are relatively sluggish on water oxidation reaction (WOR) and oxygen reduction reaction (ORR), contributing a large fraction of polarization to the total cell

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

resistance.[29-30] At present, the oxygen electrodes used in PCECs originated from the cathodes in solid oxide fuel cells without complete consideration of the required material parameters. When the operating temperature is decreased to 500~600 °C, the oxygen electrode still contributes a great polarization resistance to both fuel cell and electrolysis operation. In addition, the chemical stability of the electrode and electrolyte/electrode bonding strength, particularly in high steam concentration, can also challenge the performance durability. Therefore, the development of a highly active oxygen electrode with abundant active sites for catalytic reactions is essential for improving electrochemical performance with high stability under operation at high steam concentrations.[31]

For the high-temperature SOCs, the common strategy for the selection of oxygen electrode is to use mixed ionic and electronic conducting oxides which possess good electrical conductivity for extending the active triple-phase boundary area for the reaction.[32-34] One of the promising electrodes originates from the layered perovskite structure with fast surface kinetics and bulk diffusion, e.g. $PrBa_{0.5}Sr_{0.5}Co_{2-x}Fe_xO_{5+\delta}$ (PBSCF) which shows the potential of being applied for fuel cell or electrolysis operation at reduced temperatures.[35] For layered perovskite type oxides with composition formula of $LnBaCo_2O_{5+\delta}$ (Ln = Gd, Pr, Y, La, etc.),[36-38] the structure can be written as $A'A''B_2O_6$ by doubling the unit cell of ABO_3 perovskite, and consists of repetitive layers $[A'O_\delta]$ - $[BO_2]$ - $[A''O]$ - $[BO_2]$, where A', A'' and B sites are Pr, Ba, Co respectively.[39] Such ordered A cations confine and localize the oxygen vacancies into $A'O_\delta$ or rare-earth layers, which helps to enhance the high concentration of disordered oxygen vacancies, fast oxide ion mobility in the layers and the high electronic conductivity.[40-41] Recently, Liu et al. reported a layered perovskite $PrBa_{0.8}Ca_{0.2}Co_2O_{6-\delta}$ (PBCC) with excellent oxygen reduction activity and high tolerance against high CO_2 concentration for solid oxide fuel cell with oxide-ion conducting doped ceria electrolyte,[42] which has demonstrated the potential of this material being utilized in PCEC. To further enhance the catalytic activity towards WOR and ORR, increasing the intrinsic oxygen vacancy concentration by introducing cation deficiency is a path to obtain higher oxygen diffusivity and surface defects for the reaction.[43] There have been several studies to prove that the introduction of A-site deficiency in perovskite can significantly enhance the diffusion of lattice oxygen and hence improve catalytic activity.[44-45] For example, A-site deficient $(La_{0.6}Sr_{0.3})CrO_3$ anode material shows 4 times higher peak power density than normal $(La_{0.7}Sr_{0.3})CrO_3$ at 800 °C due to the promoted ion diffusion.[46] The electrochemical ORR activity has been also promoted for cation deficient $Sr_{0.95}Co_{0.8}Nb_{0.1}Ta_{0.1}O_{3-\delta}$ cathode which displayed about 1.5 times higher peak power density than the stoichiometric $SrCo_{0.8}Nb_{0.1}Ta_{0.1}O_{3-\delta}$ because of its higher oxygen vacancy concentration.[47] Another study shows that the introduction of both Pr^{3+} and Ba^{2+} deficiency into $PrBaCo_2O_{6-\delta}$ oxygen electrode could decrease polarization resistances and activation energy hence the electrochemical performance is significantly improved.[48] Inspired by the role of A-site deficiency in changing oxygen non-stoichiometry for improving activity, in this work, a novel layered perovskite structure with A-site deficiency in PBCC, namely $(PrBa_{0.8}Ca_{0.2})_{0.95}Co_2O_{6-\delta}$ (PBCC95), was synthesized and studied as oxygen electrode material for PCECs. When this material is integrated into PCECs, the cell demonstrates superior electrochemical performances in both fuel cell and electrolysis modes. The effects of A-site deficiency on the oxygen vacancy concentration, electrode polarization resistance and cell performance were evaluated to investigate the role of created A-site deficiency in improving the performance and long-term stability in PCEC operation. In addition, the excellent reversible operation was also successfully demonstrated, which represents a good dynamic mode transition enabled by this new electrode with fast adaption to both WOR and ORR at reduced temperatures.

Experimental

Materials

Praseodymium(III) nitrate hexahydrate ($Pr(NO_3)_3\cdot 6H_2O$, 99.9% purity), barium nitrate ($Ba(NO_3)_2$, ≥99% purity), and calcium nitrate tetrahydrate ($Ca(NO_3)_2\cdot 4H_2O$, >99% purity) were purchased from Sigma-Aldrich. Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$, 99% purity), citric acid ($C_6H_8O_7$, 99.5% purity), and glycine ($NH_2CH_2CO_2H$, 99% purity) were purchased from Alfa Aesar.

Synthesis of PBCC and PBCC95 electrode powder

Double-layered perovskite PBCC and PBCC95 powders were synthesized by the wet-chemistry self-combustion method. Stoichiometric amounts of metal nitrates were mixed in deionized water to form a clear precursor solution with concentration ~0.05 mol L^{-1}. The glycine and citric acid functioning as the complexing agent and fuel for the following combustion were added in the precursors nitrates solution with a mole ratio of glycine: citric acid: cations = 2:1:1. The precursor solution was then heated on a hot plate with magnet stirring to evaporate water. When the water was totally evaporated to form the gel that was further heated to about 350 °C. Finally, the gel underwent an auto-ignition process, which produced a voluminous powder ash. The formed ash was then fired at 1100 °C for 4 h to obtain crystallized double-layer perovskite phase.

Characterizations

The phase structure of PBCC and A-site deficient PBCC95 were determined by X-ray powder diffraction (XRD, 2008 Bruker D8). The microstructure and morphology of the PBCC95 powder was examined using a scanning electron microscope (SEM, JEOL 6700F) and transmission electron microscopy (TEM, JEOL 4000 EX). Energy-dispersive X-ray spectroscopy (EDX) mapping was used to investigate element distribution. Selected area electron diffraction (SEAD) pattern was applied to demonstrate the crystal nature. Thermogravimetric analysis (TGA, Q500 TA instruments) was carried out to study the weight loss for determining the behaviour of oxygen deficiency. The 50 mg of PBCC95 powder was placed on an alumina holder and then heated in air from room temperature to 650 °C with a ramping rate of 10 °C min^{-1}. For oxygen temperature-programmed desorption (O_2-TPD) experiment, 0.1 g powder was pre-treated at 500 °C in oxygen for 2 h. After cooling down, the Ar gas was purged for 1 h to remove the oxygen residues on the surface. Then the desorbed oxygen species were in-situ analysed with mass spectroscopy as the reactor was heated to 850 °C with a ramping rate of 4 °C min^{-1}.

Fabrication of Symmetrical Cells and PCEC Cells

To prepare the symmetric cells, the $BaCe_{0.4}Zr_{0.4}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb4411) electrolyte pellets were firstly fabricated by uniaxially pressing the powders to form the green pellets for high-temperature sintering at 1450 °C for 4 h to be densified. The PBCC and PBCC95 electrode slurries were prepared by dispersing the respective powders into the binder (butyl carbitol acetate) and ethanol with ball-milling for 10 min. The slurry was then mixed and deformed to be a thick sticky slurry by a planetary centrifugal mixer (Thinky mixer ARE-310). The electrolyte pellet was 0.5 inche in diameter. The working electrode and counter electrode were 0.25 inch and symmetrically print on two sides of a BCZYYb4411 electrolyte pellet in the centre. Silver paste was used as the reference electrode on the side of working electrode with no connection to the working electrode. Silver wires were used to connect to electrochemical workstation (Solartron 1400). The configuration of a 3-electrode symmetrical cell was shown in Fig. S1. The electrode slurry was respectively screen painted onto both sides of the electrolyte pellet for firing at 1000 °C for 4 h to form the symmetric cell with the porous PBCC electrode with an active area of 0.178 cm^2. For the preparation of full cells, the NiO/BCZYYb4411 hydrogen electrode and electrolyte green tapes were firstly fabricated by tape casting method. The combined layers of the electrode support and the electrolyte membrane were laminated at 70 °C for overnight to form the half-cell green tapes. The cells were cut out of the tapes with a diameter of 0.5 inches and pre-sintered at 920 °C to remove the organic solvents. Finally, the cells were sintered at 1450 °C for 6 h to densify the electrolyte. Then the PBCC (or PBCC95) electrode was sintered onto the electrolyte by firing it at 1000 °C for 4 h to obtain the final full cells with an active area of 0.178 cm^2.

Electrochemical performance measurement and post-test examination

The area specific resistances (ASR) of PBCC and PBCC95 electrodes at 500~600 °C in symmetrical cells with a three-electrode configuration were measured under open circuit voltage (OCV) condition and a bias current of -0.1 A cm^{-2} to study the activity at both fuel cell and electrolysis modes. The effect of current bias on the electrode resistance was studied by measuring impedance at 600 °C when the bias on the sample in oxygen was increased from 0 to -0.2 A cm^{-2}. To investigate the ASR dependency on the oxygen partial pressure, the impedance was also measured at 600 °C when the gas condition was changed from 0.05 to 1.0 atm for oxygen partial pressure (P_{O_2}).The electrode stability was examined in 20% steam concentration for 200 h while the symmetric cell was applied with current density of -0.05 A cm^{-2} at 600 °C. For the full cell testing, the as-fabricated button cell was sealed with ceramic sealant (Ceramabond 552) onto the testing fixture and the electrochemical performances in both electrolysis and fuel cell modes were collected by electrochemical working station (Solartron 1400). Electrochemical impedance spectra (EIS) was measured at OCV and 1.3 V with frequency from 10^5 to 0.1 Hz and AC amplitude of 20 mV. Reversible operation between electrolysis and fuel cell mode at 550 °C was investigated by switching the voltage to enable the dynamic operation. The long-time stability was examined for 160 h when the temperature was fixed at 500 °C with electrolysis voltage of 1.3 V and fuel cell voltage of 0.7 V. After the electrochemical testing, the microstructure of the button cells was observed using a SEM in back scattering electron mode.

Results and discussion

Characterization of PBCC95

Ordered double perovskite $AA'B_2O_{6-\delta}$ is featured with A-site ordered in alternating octahedra along the c-axis. As shown in Fig. 1a, the Pr and Ba/Ca ions in PBCC alternately occupy the interstitial sites surrounded by CoO_2 octahedra. When the A-site is deficient by adjusting the A/A' stoichiometry to 0.95 during synthesis to obtain PBCC95, more oxygen vacancies can be generated due to charge neutrality besides thermally activated vacancies. These extra oxygen vacancies are able to transport in the PrO layer with fast diffusion kinetics due to the ordered A-site structure, which has been extensively studied in other layered perovskites.[49] To confirm the phase structure of PBCC and PBCC95, the XRD patterns (Fig. 1b) show a pure layered perovskite identified to space group *P4/mmm* which is consistent with the literature.[32, 50] There was no peaks shifted or corresponding to any impurities, indicating that 5% A-site deficiency does not result in the change of primary lattice structure. The oxygen non-stoichiometry (δ) of PBCC and PBCC95 at room temperature are determined by iodometric titration to be 0.05 and 0.3 respectively, indicating the large increase of oxygen vacancy (Fig. 1c). The oxygen non-stoichiometry in operating temperatures is calculated by obtaining the oxygen loss from the TGA result measured in air when the temperature is increased up to 650 °C (Fig. S2). The results show that the δ value of PBCC and PBCC95 increases from 0.098 and 0.342 at 500 °C to 0.142 and 0.386 at 600 °C, respectively. Both PBCC and PBCC95 have increased oxygen vacancy concentration over elevated temperatures and the A-site deficient PBCC95 electrode possesses higher non-stoichiometry, which facilitates the enhancement of electro-activity towards the water splitting and oxygen reduction reaction.[51-52] Furthermore, the resulting catalytic activity due to the enhanced vacancy

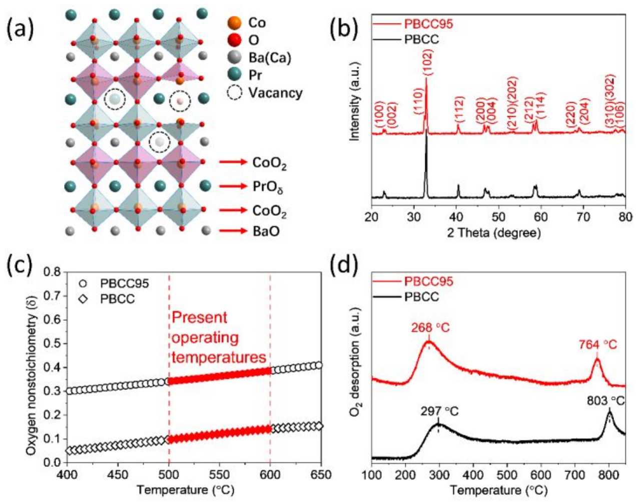

Fig. 1. Material characterization of PBCC and PBCC95 electrodes. (a) schematic of crystal structure for PBCC double perovskite with A-site deficiency; (b) XRD patterns of PBCC and PBCC95; (c) the oxygen non-stoichiometry of PBCC and PBCC95 in temperatures between 400 and 650 °C; (d) O_2-TPD profiles of PBCC and PBCC95.

concentration has been examined by O_2-TPD to analyze the activity of respective oxygen species (chemisorbed/lattice oxygen atoms) during the dissociation process in electrode surface and bulk. Fig. 1d shows the spectrum of oxygen desorption in a temperature range of 100~850 °C. The desorption signal at temperatures below 400 °C (denoted as α-O) relates to the chemisorption of oxygen (O^{2-} or O^{-}) due to weak bond with the surface.[53] The second signal at the temperature higher than 400 °C is ascribed to the loss of lattice oxygen (denoted as β-O).[54] The α-O peak of PBCC95 is observed at 268 °C, which is 29 °C lower than that of PBCC (297 °C), and PBCC95 also shows a lower β-O desorption peak at 764 °C comparing to PBCC (803 °C). The lower oxygen desorption temperature indicates that the higher oxygen diffusivity and surface activity in PBCC95 electrode which can be obtained to improve the catalytic activity.[51, 55-56]

The morphology, lattice structure and element distribution of the synthesized PBCC95 electrode are shown in Fig. 2. After calcining at 1100 °C, the fine powders have diameter less than 1 μm. High resolution TEM (HR-TEM) image shows the good crystallization nature with the interplanar lattice distance of 0.383 nm (Fig. 2b), responding to (002) crystal plane, which is about a half of the distance between PrO or BaO planes (0.762 nm).[42] The inset shown in Fig. 2b is the SAED pattern of a single PBCC95 particle, which shows a single crystal diffraction character. The distance of the spots is measured and calculated. It is found that the diffraction pattern corresponds well to the PBCC95, this result is in well agreement with the above XRD.

This result indicates that introducing a minor A-site deficiency has no observable effect on the double perovskite structure. The SAED pattern exhibits a single crystal structure and the interplanar lattice distances consistent with the XRD and HR-TEM results. The uniform distribution of the cations and oxygen is confirmed by EDX mapping on a single particle (Fig. 2c).

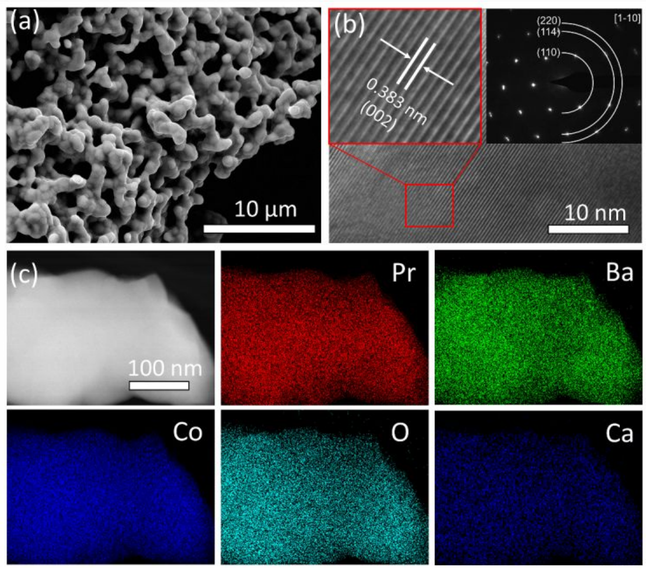

Fig. 2. Morphology and lattice structure of PBCC95 electrode. (a) SEM image of PBCC95 powder; (b) HR-TEM image of PBCC95 particle; (inset) SEAD pattern of PBCC95; (c) EDX-mapping of a PBCC95 particle.

Electrochemical performance of PBCC95 electrode

To evaluate the improvement of electrochemical activity for the PBCC electrode after adopting cation deficiency, the symmetric cells are prepared to compare the electrode polarization resistance (R_p) by impedance measuring with the three-electrode configuration. The 3-electrode testing can effectively mitigate the effects from the counter electrode, ensuring a specific reaction to be studied. The impedance spectra in Nyquist plots and fitting results for PBCC and PBCC95 measured at open circuit in wet oxygen (3% H_2O) and 600 °C are depicted in Fig. 3a. The spectra can be separated into two arcs located in the high-frequency zone (HF, 10~500 Hz) and the low-frequency zone (LF, 0.1~10 Hz). These spectra can be fitted well to the equivalent circuit R_{ohm}-(R_{HF}-CPE_{HF})-(R_{LF}-CPE_{LF}) as shown in the inset figure. As identified in other studies, the LF part is regarded as the process of oxygen diffusion while HF part originates from oxygen dissociation in the electrode.[57-58] The R_{HF} and R_{LF} of PBCC are 0.058 Ω cm² and 0.162 Ω cm², respectively, while PBCC95 shows a 41% smaller R_{HF} (0.034 Ω cm²) and 35% smaller R_{LF} (0.106 Ω cm²) compared to PBCC. This decreasing trend of R_{HF} and R_{LF} indicates the enhanced kinetics and activity of PBCC95 electrode, which results from the increased oxygen vacancy introduced by the A-site deficiency. Fig. 3b shows the Arrhenius plot of overall R_p obtained under open-circuit condition from fitted EIS as a function of temperature in pure oxygen. The activation energies of PBCC and PBCC95 are 1.21 eV and 1.12 eV, respectively. The activation energies are calculated by the following equation:

$$\mathrm{R_p} = \mathrm{R_p^0} e^{-\frac{\mathrm{E}_a}{\mathrm{RT}}} \qquad (1)$$

Where R is the gas constant 8.314 J mol^{-1} K^{-1}; E_a is the activation energy; T is the temperature.

Smaller activation energy of PBCC95 indicates the higher electrochemical activity toward oxygen reduction in equilibrium state at lower temperatures. This result has shown that the A-site deficiency can increase the catalytic activity by generating more oxygen defects in both surface and bulk.[43] Furthermore, the effect of applied electrolysis current density on EIS has been studied and shown in Fig. 3c. It can be clearly seen that the PBCC95 shows an obvious trend of decreasing R_p when the applied current density increases from 0 to -0.2 A cm^{-2}. Fig. S3 depicts that the decreasing of PBCC95 R_p results from both HF and LF arcs, indicating the enhanced electrode reaction kinetics on the surface under the applied electrolysis current density.

As the applied current largely affects the R_p, PBCC and PBCC95 oxygen electrodes behaviours in electrolysis mode are also evaluated in three-electrode symmetric cells. Fig. 3d shows the dependence of electrode polarization resistance on the operating temperature when the sample is exposed to humid oxygen (~3 % H_2O) and applied with bias current density of -0.1 A cm^{-2}. When the temperature is increased, the R_p for PBCC increases from 0.084 Ω cm² at 600 °C to 0.191 Ω cm² at 550 °C and 0.298 Ω cm² at 500 °C, respectively. For PBCC95, the comparison clearly demonstrates a decreased R_p, e.g., 0.065 Ω cm² at 600 °C, which has decreased by 23% from 0.084 Ω cm² for PBCC. The calculated activation energy with bias electrolysis current density of -0.1 A cm^{-2} for PBCC95 is 1.25 eV, which is decreased from 1.32 eV for PBCC. The smaller activation energy of PBCC95 under -0.1 A cm^{-2} applied current indicates the higher anodic electrochemical activity in steady-state, and the A-site deficient PBCC95 is kinetically more favorable than PBCC in electrolysis mode.

To evaluate the effect of other operating conditions on the oxygen electrode activity in electrolysis mode, the dependence of R_p on various oxygen partial pressure (balanced by Ar) is shown in Fig. 3e. As P_{O_2} increased from 0.05 to 1.0 atm, R_p of PBCC95 is decreased from 0.94 to 0.065 cm^2 at 600 °C and applied electrolysis current of -0.1 A cm^{-2}. PBCC shows similar trend of decreasing R_p from 1.06 Ω cm^2 to 0.086 Ω cm^2. The result is attributed to the improved electrical conductivity in the higher P_{O_2} and indicates that higher oxygen content is preferred in the electrolysis operation. In addition, the stability of the electrode activity in the 20% steam concentration has been examined (Fig. 3f). A constant current density bias of -0.05 A cm^{-2} is applied to the cell and the R_p is measured every 10 h. As can be seen, the R_p value is stable over 200 h without observable degradation, demonstrating the robust stability in the material structure and interfacial strength of this PBCC95 electrode with the electrolyte.

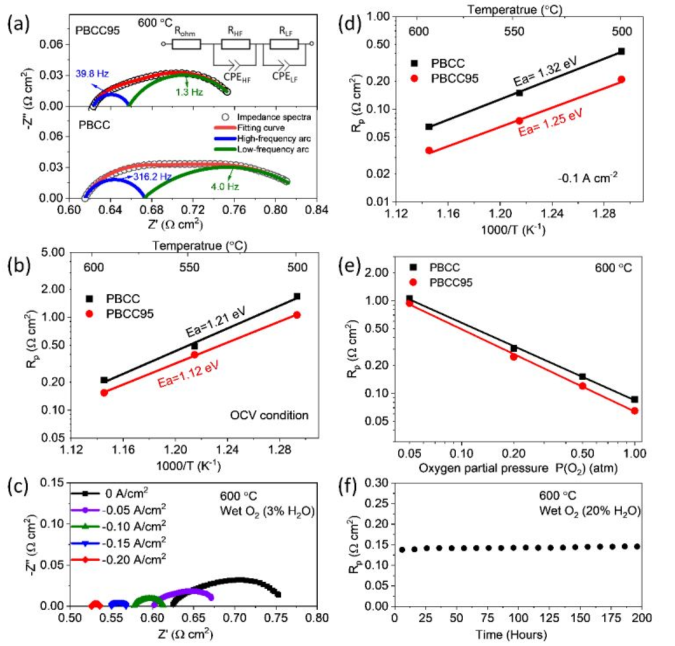

Fig. 3. Performance of PBCC and PBCC95 in symmetric cells with 3-electrode configuration. (a) EIS and fitted spectra of PBCC and PBCC95 tested at 600 °C; (inset) equivalent circuit used fitting; (b) Arrhenius plot of R_p for PBCC and PBCC95 between 500 °C and 600 °C under OCV condition; (c) the effect of applied electrolysis current density on the electrode polarization measured by AC impedance spectra at 600 °C for PBCC95 electrode. (d) Arrhenius plot of R_p for PBCC and PBCC95 between 500 °C and 600 °C under applied electrolysis current density of -0.1 A cm^{-2}; (e) dependence of R_p as a function of P_{O_2} tested at 600 °C and -0.1 A cm^{-2}; (f) stability of PBCC95 electrode resistance in humidified oxygen (~20% H_2O) at 600 °C and -0.05 A cm^{-2}.

Electrochemical performance of the PCEC with PBCC and PBCC95 electrode

To further demonstrate the catalytic activity improvement by the A-site deficiency manipulation, the PCECs with PBCC95 and PBCC as oxygen electrode and BCZYYb4411 as electrolyte have been fabricated and measured. The performance in fuel cell mode has been examined when wet hydrogen (~3% H_2O) and oxygen are fed into anode and cathode side, respectively, to demonstrate the activity towards ORR. The use of pure hydrogen can facilitate the examination of cell quality and performance comparison with other works. As shown in Fig. 4a, the OCVs reach 1.06 V at 600 °C, 1.09 V at 550 °C and 1.12 V at 500 °C, respectively, which are close to the theoretical Nernst potentials of 1.165 V, 1.171 V and 1.178 V, respectively.[59-60] These high voltages indicate high density of electrolyte membrane and good cell sealing. The peak power densities of A-site deficient PBCC95 are 0.540, 0.354 and 0.222 W cm^{-2} at 600, 550 and 500 °C, respectively. The cell with PBCC electrode shows peak power density of 18.7%, 20.9%, and 23.8% lower than PBCC95 at 600, 550 and 500 °C, respectively (Fig. 4b). The higher fuel cell performance indicates the increased ORR activity due to the abundant oxygen vacancies and fast kinetics of PBCC95.

Fig. 4c shows the current-voltage (I-V) curves of electrolysis performance in temperature range of 500~600 °C with humidified oxygen (~20%) in oxygen electrode. Pure hydrogen is used in the hydrogen electrode to avoid gas separation and help maintain a high OCV. The cell with PBCC95 electrode shows much higher performance than the one with PBCC electrode at the same operating conditions. For example, the current densities of PBCC95 cell at 600 °C are -0.72 A cm^{-2} at 1.3 V and -1.33 A cm^{-2} at 1.4 V, respectively, performing 30.1% higher than PBCC with -0.505 A cm^{-2} at 1.3 V and 22.0% higher at 1.4 V. At lower temperatures of 550 and 500 °C, the current density of PBCC95 cell can still reach -0.39 A cm^{-2} and -0.16 A cm^{-2} at 1.3 V, which are 33.9% and 50.7% higher than PBCC performance as shown in Fig. 4d. The superior performance of this cell is among the highest performances of PCECs up to date. For example, Norby et al. have recently demonstrated a double perovskite as oxygen electrode in PCEC with the electrolysis current density less than -0.1 A cm^{-2} with considerable efficiency at 1.3 V and 600 °C.[61] Liu et al. have reported a triple-conducting Ruddlesden-Popper (R-P) structured perovskite $Pr_2NiO_{4+\delta}$ as electrode in PCEC with less than -0.4 A cm^{-2} at 1.3 V and 600 °C.[62] Li et al. have reported a R-P perovskite $La_{1.2}Sr_{0.8}NiO_4$ in PCEC with current density measured to be -0.42 A cm^{-2} at 1.3 V and 600 °C.[63] The PBCC95's performance is also comparable to Kim's work in which a hybrid PCEC with mixed proton and oxide-ion conducting $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ electrolyte and electrolysis current density of -0.75 A cm^{-2} at 1.3 V and 600 °C.[64]

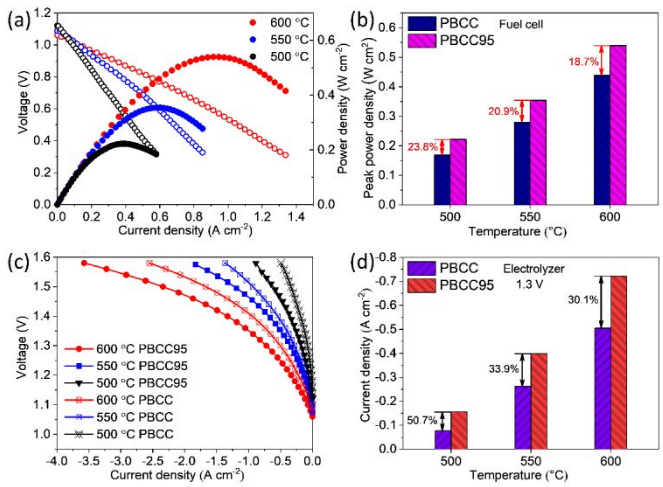

Fig. 4. Electrochemical performances of PBCC95 and PBCC electrodes at 500, 550, and 600 °C. (a) I-V and current-power density (I-P) curves of PBCC95 in fuel cell mode; (b) peak power density comparison between PBCC95 and PBCC; (c) I-V curve of PBCC95 and PBCC electrodes in electrolysis mode; (d) Electrolysis current density comparison of PBCC95 and PBCC at 1.3 V.

Therefore, the PBCC95 represents a promising oxygen electrode material for electrolysis cell. The improvement of electrolysis performance has been studied by EIS as shown in Fig. S4. At 600 °C and 1.3 V, R_p of the cell with PBCC95 electrode is 0.024 Ω cm^2, which is 53.8% smaller than the R_p for PBCC electrode. Similarly, the PBCC95 also performs much better than PBCC at lower temperatures. At 550 and 500 °C, the R_p is accordingly decreased by 55.8% and 52.4% respectively. Furthermore, the performance stability at different electrolysis voltages of 1.2 V, 1.3 V, 1.4 V and 1.5 V was examined at 600 °C, as shown in Fig. S5a. The initial current densities are -0.37 A cm^{-2}, -0.72 A cm^{-2}, -1.33 A cm^{-2}, and -2.36 A cm^{-2} respectively. At each voltage point, the cell shows a slight improvement in current density, which may be attributed to the process of electrode activation.[35, 65] After the durability testing, the R_p value decreases from 0.025 Ω cm^2 to 0.017 Ω cm^2 as shown in Fig. S5b, indicating the improved electrode interface. The results demonstrate that PBCC95 shows better performance than PBCC in both fuel cell and electrolysis modes due to the higher catalytic activity resulting from A-site deficiencies.

To demonstrate the feasibility of the reversible operation between electrolysis mode and fuel cell mode, it is critical to evaluate the performance of this PBCC95 electrode in a dynamic cycling transition process in a fast manner. As shown in Fig. 5a, the cell is operated in electrolysis voltage of 1.3 V for 5 minutes to produce hydrogen, and then switched to fuel cell voltage of 0.8 V to generate electricity for another 5 minutes at 550 °C. Then the cell is operated at higher current densities by increasing electrolysis voltage to 1.4 V and 1.5 V and reducing fuel cell voltage to 0.7 V and 0.6 V for examining the working flexibility. For each test, the cell is cycled 10 times. The smooth transition between each mode and the stable current densities indicate that PBCC95 electrode can work for water splitting and oxygen reduction reactions stably and adapt to each mode quickly. When the cell is transitioned to a new mode by adjusting the voltage to three increasing electrolysis voltages and then to three decreasing fuel cell voltages, the responding current densities were still stable. This complex operation can demonstrate the high reversibility of PBCC95 on two different electrochemical reactions of water oxidation and oxygen reduction. Furthermore, the durability of the cell has been examined in both fuel cell mode and electrolysis mode at 500 °C for 160 h. As shown in Fig. 5b, in electrolysis mode the current density at 1.3 V is about -0.16 A cm^{-2}, while in fuel cell mode the current density at 0.7 V is about 0.30 A cm^{-2}, which shows good durability in both operating modes with no observable degradation.

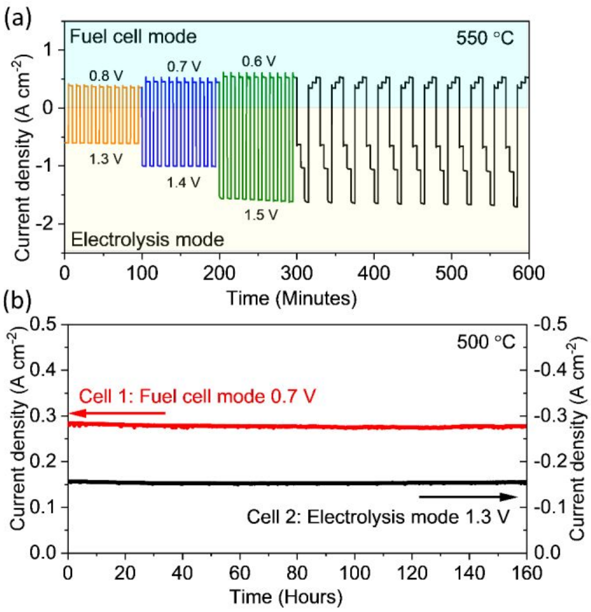

Fig. 5. Reversible operation of the electrochemical cell and long-term stability in fuel cell and electrolysis modes. (a) Reversible operation between electrolysis and fuel cell mode at 550 °C when the cell working voltage is transiently changed; (b) long-term stability testing of the cell in fuel cell mode at 0.7 V and in electrolysis mode at 1.3 V and 500 °C.

After all the electrochemical testing, the post-mortem cell is examined by SEM and shown in Fig. 6. The BCZYYb4411 electrolyte surface is dense without any defects (pinhole/impurity) observed, which prevents gas leakage. After the testing, the reduced hydrogen electrode is composed of porous nickel particles and dense electrolyte particles in uniform distribution between the metal and ceramic phases from the cross-section view (Fig. 6b). The electrolyte is fully dense with thickness about 20 μm and adheres well to both electrodes without delamination observed at interfaces. The flower-like morphology nickel particles in the magnified hydrogen electrode SEM (Fig. 6c) indicate the complete reduction from NiO to Ni metal. In oxygen-electrode/electrolyte interface (Fig. 6d), the PBCC95 shows porous structure consisting of small particles and adheres to the electrolyte membrane strongly, which ensures the fast gas diffusion and little degradation on the interface during operation.

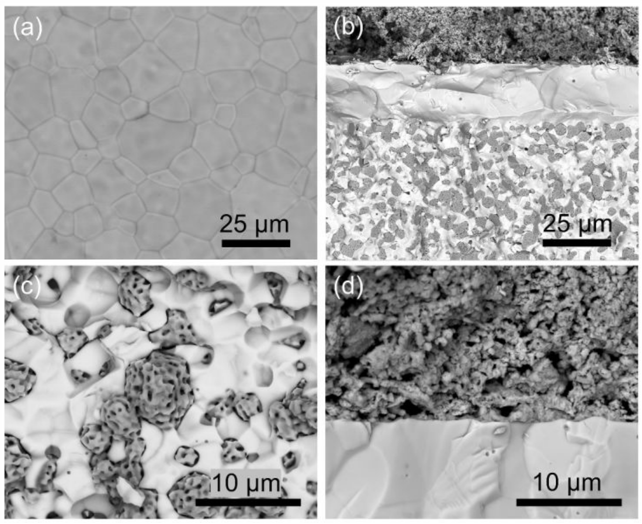

Fig. 6. The morphology of the post-mortem cell. (a) SEM image of electrolyte surface; (b) cross-section image of the interface with PBCC95 oxygen electrode, BCZYYb4411 electrolyte, and Ni/BCZYYb4411 hydrogen electrode; (c) magnified SEM image in hydrogen electrode with flower-like nickel particles; (d) electrolyte/PBCC95 electrode interface.

Conclusions

A-site cation ordered and deficient PBCC95 was successfully synthesized and studied as the oxygen electrode in PCECs for fuel cells and hydrogen production. This novel electrode exhibited great advantage of increased catalytic activity towards water oxidation and ORR compared to PBCC without A-site deficiency. At intermediate temperatures, the PCEC with BCZYYb4411 electrolyte and PBCC95 electrode showed high and stable electrochemical performance and reversible operation. A high electrolysis current density of -0.72 A cm^{-2} at 1.3 V and a peak power density of 0.540 W cm^{-2} were achieved at 600 ^{o}C. The fast-reversible operation in transiently varied voltages between electrolysis and fuel cell mode demonstrated the feasibility of this PBCC95 electrode of switching role in water oxidation and oxygen reduction. The long-term durability testing at 500 ^{o}C proved the chemical and interfacial stability during the electrolysis and fuel cell process for 160 h.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

This work is supported by the U.S. Department of Energy (USDOE), Office of Energy Efficiency and Renewable Energy (EERE), Fuel Cell Technologies Office (FCTO) under DOE Idaho Operations Office under contract DE-AC07-05ID14517.

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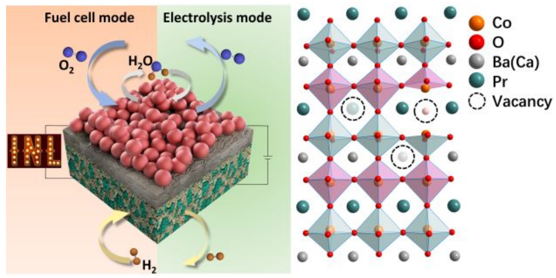

An A-site deficient layered perovskite PBCC95 is developed as a new oxygen electrode incorporated into protonic ceramic electrochemical cell. The cell presents superior electrochemical performances and it can reversibly work between electrolysis and fuel cell mode.