Electrochemical performance of double perovskite Pr$_2$NiMnO$_6$ as a potential IT-SOFC cathode

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ABSTRACT

Double perovskite oxide Pr$_2$NiMnO$_6$ is evaluated as a potential cathode for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The reactivity test indicates that no reaction occurs between Pr$_2$NiMnO$_6$ and CGO at 1200 °C in air. The thermal expansion coefficients (TEC) of Pr$_2$NiMnO$_6$ are 10.6 × 10$^{-6}$ K$^{-1}$ in air and 11.5 × 10$^{-6}$ K$^{-1}$ in nitrogen atmosphere within a temperature range of 100–800 °C. The electrochemical properties of Pr$_2$NiMnO$_6$ cathode are characterized by ac impedance and dc polarization methods, respectively. The lowest area specific resistance (ARS) is 0.38 Ω cm$^2$ at 700 °C in air. The dependence of ARS with oxygen partial pressure indicates that the charge transfer process is the rate-limiting step for oxygen reduction reaction on Pr$_2$NiMnO$_6$ cathode.

Introduction

One of the major challenges encountered to develop IT-SOFCs is the large cathode overpotential due to the slow oxygen reduction reaction (ORR) kinetics at intermediate temperatures (below 800 °C) [1]. In order to overcome this problem, mixed ionic and electronic conducting (MIEC) materials have been proposed. It is believed that the improved electrode properties are due to the extending of reaction sites from the traditional triple-phase-boundary (TPB) regions to the entire electrode surface [2]. Most of the works concerning MIEC materials are on simple perovskite related compounds, such as Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (BSCF) [3], La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ (LSCF) [4] and Ln$_2$NiO$_{4+δ}$ [5] et al. Recently, A cation ordered double perovskite LnBaCo$_{2}$O$_{5+δ}$ (Ln = Lanthanide) has been extensively studied as potential cathode for IT-SOFCs [6–10]. This material possesses an ordered layer-type structure with the oxygen vacancies mainly presented in Ln-O layer, which greatly enhances the oxygen transport kinetics and its electrochemical activity for oxygen reduction reaction (ORR) [11–13]. The LnBaCo$_{2}$O$_{5+δ}$ material however, similar to the other cobalt-containing cathodes, exhibits relatively large thermal expansion coefficient (TECs, above 20.0 × 10$^{-6}$ K$^{-1}$ within 100–800 °C in air) that is not compatible with most of
the well known electrolyte materials [14,15]. In this sense, it is highly recommended to develop non-cobalt cathode materials for IT-SOFCs.

B cation ordered double perovskite materials $A_2BB'O_6$ exhibit rich physicochemical properties and attractive technological applications [16–18]. The structure of $A_2BB'O_6$ oxides can be derived from the simple perovskite $AB'O_3$, where the B-sites are alternately occupied by two different cation species (B and B'). The specific alternating arrangement of B and B' cations in $A_2BB'O_6$ can be of great interest from the catalytic point of view, since the electrocatalytic properties are generally determined by the nature, oxidation states and the relative arrangement of B-site cations [19]. These materials have been recognized as potential anode for solid-oxide fuel cells that operating on natural gas as the fuel [20]. However, there are very few reports about B cation ordered double perovskite as the cathode for high-temperature devices [21,22]. In order to explore the feasibility of non-cobalt cathode materials, we intend to investigate the high-temperature electrochemical properties of B cation ordered double perovskite material $A_2BB'O_6$ with Ni and Mn locating alternatively in B and B' site. The selection of Ni and Mn as B site ions are based on the following considerations: 1). research has found that the oxygen vacancy formation energy of the double perovskite $A_2BB'O_6$ is based mainly on the strength of B(B')-O bond, and the delocalized rearrangement of the extra charge delivered to the lattice upon removal of the neutral oxygen atoms [23]. These findings indicate that the perovskite enriched with late transition metals to weaken the transition metal-oxo bonds and thus enhance metal d–O p hybridization will promote the oxygen reduction reaction (ORR). 2). Ni and Mn based perovskite materials have been extensively studied as promising cathodes in SOFCs, due to the multivalent characters of Ni and Mn elements, and the generation of oxygen vacancy in the lattice. It is well-known that the cation valence state and the oxygen vacancy concentration play important roles in the physical and electrochemical properties of the double perovskite materials [24]. In this paper, $Pr_2NiMnO_6$ was prepared and the electrical conductivity, chemical compatibility and electrochemical properties were systematically studied.

### Experimental

#### Sample preparation

$Pr_2NiMnO_6$ (PNMO) powder was synthesized by the conventional solid–state reaction method. Analytical grade $Pr_2O_3$, NiO and MnCO$_3$ were taken in a stoichiometric ratio and were homogeneously mixed using an agate mortar for approximately 30 min. The resulting mixture was pressed into pellets, and then calcined consecutively at 1000 °C, 1200 °C and 1400 °C for 24 h in air with a ramp rate of 10 °C min$^{-1}$. After calcination, the pellet was crushed and followed by repeated grinding and calcination until complete reaction was achieved. The obtained PNMO was mixed with $Ce_0.5Gd_0.5O_{1.95}$ (CGO) in a 50/50 weight ratio, and sintered at 1200 °C for 12 h in air to check the chemical compatibility.

The CGO powder was pressed uniaxially under 220 Mpa and sintered at 1400 °C for 10 h to obtain dense electrolyte substrates with 10.5 mm in diameter and 0.8 mm in thickness. The cathode ink was prepared by thoroughly mixing the PNMO powder with terpineol for several hours. The symmetrical cell PNMO/CGO/PNMO was fabricated by manually brushing PNMO ink on both sides of the polished CGO pellet to form a square electrode with an effective area of 0.25 cm$^2$. The cell was then sintered in air at 950 °C, 1050 °C and 1150 °C for 4 h, respectively. Fine platinum gauzes were slightly pressed on both sides of the cell as current collectors. For three electrodes cell, the PNMO ink was painted on one side of the CGO pellet to act as a working electrode (WE). Pt-paste was painted on the opposite side of the CGO pellet in symmetric configuration, and then sintered at 800 °C for 1 h in air, to form the counter electrode (CE). A Pt wire was used as reference electrode (RE) and put on the same side of the working electrode.

#### Characterizations

The structure of PNMO was analyzed by powder X-ray diffraction (Cu K$\alpha$, 20–80°, 0.02°/step). The morphology and microstructure of the sintered electrodes were examined by field emission scanning electron microscope (FEG-SEM, Hitachi S-4700) at an accelerating potential of 20 KV. The electrical conductivity of the sample was measured from room temperature to 800 °C by a DC four-probe method. The X-Ray photoelectron spectroscopy (XPS) was acquired using AXIS ULTRA DLD instrument to analyze the surface chemistry of PNMO. The thermal expansion coefficient (TEC) of the sample was measured with TMA system (SETSYS Evolution, France) from room temperature to 800 °C in air and in nitrogen atmosphere, respectively. The impedance spectrum of the cell was recorded over the frequency range 1 MHz to 0.01 Hz using Autolab PGStat30. The measurements were performed at OCV as a function of temperature (500–700 °C) and oxygen partial pressure (in N$_2$/O$_2$ mixed atmosphere).

#### Results and discussion

### Characterization and chemical compatibility

Fig. 1(a) shows the XRD patterns of PNMO. It is characterized by a series of sharp peaks, revealing that the product is polycrystalline in nature. The Rietveld refinement result (Fig. 1a) reveals that PNMO crystallizes in monoclinic structure (space group P2$_1$/n), and the obtained cell parameters are $a = 5.426(0)$ Å, $b = 5.451(5)$ Å, $c = 7.696(6)$ Å and $\beta = 89.95(5)^\circ$, with a weight-profile R-factor (Rwp) of 10.32% and profile-fitting R-factor (Rp) of 8.40%. The cell parameters are identical to the values reported in literature [25], which means that the double perovskite $Pr_2NiMnO_6$ has been successfully prepared. The high temperature chemical compatibility of PNMO with the traditional electrolyte materials YSZ and CGO are further investigated, and the results are presented in Fig. 1(b). Clearly all the diffraction peaks can be exclusively related to PNMO and CGO phases in the heat-treated PNMO-CGO mixtures. There are no new peaks identifiable or shift of XRD peaks in the patterns, indicating that there is no obvious chemical reaction between PNMO and CGO even at 1200 °C for 12 h. For the PNMO-YSZ mixture however, additional diffraction peaks can be
observed, due to the formation of NiO and Pr$_2$Zr$_2$O$_7$ phases in the mixture (Fig. 1b). Therefore it is concluded that Pr$_2$NiMnO$_6$ is chemical compatible with CGO electrolyte at high temperatures in air.

X-Ray photoelectron spectroscopy was used to study the chemical state of the composition elements and the surface properties of the material. The wide scan XPS spectrum of PNMO demonstrates the presence of Ni and Mn elements. To understand the chemical oxidation states of Ni and Mn elements, core level spectra were recorded and the results are presented in Fig. 2(a–b). For Mn 2p spectra of PNMO, the broad peaks at 652 and 641 eV are assigned to Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$, respectively (Fig. 2a). Adam T et al. reported the peaks of binding energy of Mn$^{3+}$ 2p$_{1/2}$ and Mn$^{4+}$ 2p$_{3/2}$ at 651.9 and 640.8 eV, and Mn$^{3+}$ 2p$_{1/2}$ and Mn$^{4+}$ 2p$_{3/2}$ at 653.8 and 642.3 eV, respectively [26]. The binding energy of Mn 2p for PNMO is

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**Fig. 1** — (a) Experimental (red circles) and calculated (black continuous line) XRD patterns (and their difference, blue line at the bottom) for Pr$_2$NiMnO$_6$. Green vertical bars indicate the positions of the Bragg peaks of the phases contained in the sample; (b) The XRD patterns of Pr$_2$NiMnO$_6$ with YSZ and CGO after calcined at 1200 °C for 12 h in air. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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**Fig. 2** — XPS spectra of (a) Mn, (b) Ni and (c) Pr for Pr$_2$NiMnO$_6$. 

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different with Mn$^{3+}$ and Mn$^{4+}$, which means the Mn ion in Pr$_2$NiMnO$_6$ is in mixed valence state. For Ni 2p, the peaks of Ni 2p$_{1/2}$ and Ni 2p$_{3/2}$ are at 872 and 854 eV, respectively (Fig. 2b). Note that the peaks of binding energy of Ni$^{2+}$ 2p$_{1/2}$ and Ni$^{2+}$ 2p$_{3/2}$ at 871.64 and 853.96 eV, and Ni$^{3+}$ 2p$_{1/2}$ and Ni$^{3+}$ 2p$_{3/2}$ at 873.62 and 855.55 eV, respectively [26]. Therefore, Ni in PNMO is also in mixed valence state. For Pr 3d spectra of PNMO, the board peaks at 954 eV and 933 eV are assigned to Pr 3d$_{3/2}$ and Pr 3d$_{5/2}$, respectively. The doublet Pr3d$_{5/2}$ and Pr3d$_{3/2}$ has a shoulder at the side of lower binding energies assigned to shake-off satellites [27]. It was reported in the previous paper that the signals for Pr$^{4+}$ existed at 925.5 eV and 943.3 eV [27]. Presence of Pr$^{4+}$ was therefore not detected in the PNMO, all of Pr 3d$_{2/5}$ and Pr 3d$_{2/3}$ peaks can be attributed to the existence of Pr$^{3+}$. By fitting the XPS spectrum, the percentage contributions of the valence states and average valence states of Mn and Ni can be obtained and the results are presented in Table 1. Considering the requirement of electric neutrality condition in PNMO material, the $\delta$ value of the oxygen vacancy in the Pr$_2$NiMnO$_{6-\delta}$ is further calculated to be 0.15. The above XPS analysis demonstrates that the Mn$^{3+}$/Mn$^{4+}$ and Ni$^{3+}$/Ni$^{2+}$ couples coexist in Pr$_2$NiMnO$_6$ materials at room temperature.

**Electrical conductivity**

Fig. 4 presents the electrical conductivity of PNMO as a function of temperature. It is observed that the conductivity increases with temperature, demonstrating a semi-conducting behavior. The maximum electrical conductivity of 3 S cm$^{-1}$ is obtained at 800 °C in air. This value is much higher than the other Co-free double-perovskite material, such as La$_2$ZnMnO$_6$ [33], and comparable to that of GdBaFe$_2$O$_{5+\delta}$ [31]. From Fig. 4 it is also observed that log(\sigma T) does not exhibit the linear relationship with 1/T. An inflection point in the vicinity of 550 °C can be observed, which indicates a change of the conductive mechanism under different temperature ranges. The activation energy associated with the electrical conductivity can be obtained from the Arrhenius plots, and the calculated $E_a$ values are 0.25 (below 550 °C) and 0.36 eV (above 550 °C), respectively. Clearly from room temperature to 550 °C, PNMO exhibits a small polaron hopping mechanism. With the

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<th>Table 1 – The percentage contributions of the valence states and average valence states of Mn and Ni.</th>
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**Fig. 3** – The thermal expansion behaviors of Pr$_2$NiMnO$_6$ in (a) air and (b) nitrogen atmosphere. **Fig. 4** – Arrhenius plot of Pr$_2$NiMnO$_6$ in air.
further increase of temperature above 550 °C, the conductivity continues to increase, accompanied by the enlarging of the activation energy. This phenomenon can be ascribed to the delocalization and thermal activated mobility of the charge carriers in the lattice, which has been observed in the previous study of perovskite-type materials [34].

**Microstructure of the symmetrical cell**

To further investigate the thermal compatibility between the cathode and the electrolyte, the microstructures of the cathode on GDC electrolyte are studied by SEM. Fig. 5(a–b) shows SEM micrographs of the Pr$_2$NiMnO$_6$ cathode on the GDC electrolyte sintered at 950 °C for 4 h. The SEM images were taken from both surface and cross-section. According to the SEM micrographs, porous cathodes with the thickness ~20 μm are apparent, while the GDC electrolyte is dense. There is no obvious cracks appeared at the interface between Pr$_2$NiMnO$_6$ cathode and GDC electrolyte, suggesting a good thermal compatibility between the two materials. This kind of microstructure gives additional support for the Pr$_2$NiMnO$_6$ cathode to exhibit superior electrochemical performance.

![SEM images of the Pr$_2$NiMnO$_6$ electrode at 950 °C for 4 h](image1)

**Fig. 5** – (a) SEM images of the Pr$_2$NiMnO$_6$ electrode at 950 °C for 4 h; (b) the cross-section image of the test-cell.
Electrochemical performance

Fig. 6 presents a typical electrochemical impedance spectrum (EIS) of symmetric cell that measured under open circuit potential at 700 °C in air. Obviously only one impressed arc can be observed in the spectrum. The intercept value of the impedance arc with the real axis at high frequency corresponds to the resistance of the electrolyte and lead wires, and the value between the high-frequency intercept point of the x-axis and the low-frequency one is the total polarization resistance (Rp). Rp is widely used to describe the resistance terms related to electrode process. For the symmetrical cell, the measured Rp reflects the sum of the polarization resistance of the two electrodes investigated. Therefore the ASR can be calculated by the expression ASR = 1/2Rp·S, whereas S is the area of the cathode. The ASR value of PNMO cathode is 0.38 Ω cm² at 700 °C in air. This value is quite smaller compared to the other double perovskite cathodes. For example, the polarization resistance of Sr₂Fe₀.₁Co₀.₉NbO₆ was reported to be 0.74 Ω cm² at 750 °C in air [35]. From the Arrhenius plot of the electrode ASR (inset of Fig. 6a), the activation energy is calculated to be 1.33 eV. This value is quite similar to the reported activation energy for the interface charge transfer process [36], which is involved in the ORR reaction on cathode. Therefore, we speculate that the major reaction process on the PNMO electrode may be the interface charge transfer process.

Generally, the overall ORR reaction can be described as (1/2)O₂(g) +2e⁻ = O²⁻, while it is a complex multi-process which basically includes the gas diffusion, surface adsorption/dissociation, charge transfer reaction etc. In order to clarify the effect of oxygen partial pressure on the cathode process, a comparative study of Nyquist and Bode plots at different oxygen partial pressure were carried out. As shown in Fig. 7(a–b), clearly only one major process can be identified, and this process changes systematically with the measuring temperature and oxygen partial pressure. From the Fig. 7a, we can find that the oxygen partial pressure decreases from 0.21 atm to 0.01 atm, the ASR increases steadily from 0.38 to 1.09 Ω cm², indicating an oxygen activity related electrochemical reaction occurred on the PNMO cathode. Generally, the change of polarization resistance with the oxygen partial pressure can be defined by the following expression: Rp = R₀p × (pO₂)⁻ⁿ, and the value of n gives information about the species involved in the electrode reaction as follows:

\[ n = 1 \quad O_2(g) \rightarrow 2O_{ads} \]
\[ n = 1/2 \quad O_{ads} \rightarrow O_{TPB} \]
\[ n = 3/8 \quad O_{TPB} + e^+ \rightarrow O_{TPB}^{-1/2} \]
\[ n = 1/8 \quad O_{TPB} + e^+ \rightarrow O_{TPB}^{-1/8} \]
\[ n = 0 \quad O_{TPB} + V_0^+ \rightarrow O_x \]

n = 1 is associated with gaseous oxygen adsorptions and dissociation reaction, n = 1/2 with atomic oxygen surface diffusion to TPB site, n = 3/8 and n = 1/8 with the charge transfer process at the TPB, and n = 0 with oxygen ion transfer from TPB to the electrolyte [37–42]. The dependence of polarization resistance on oxygen partial pressure is presented in Fig. 7a (inset). The linear variation of ASR with oxygen

![Fig. 6](image_url) Fig. 6 – Nyquist plot of Pr₂NiMnO₆ cathode on CGO electrolyte measured at 700 °C in air. The inset is the Arrhenius plot of ASR.
partial pressure suggests that the rate-limiting step does not significantly depend on the oxygen non-stoichiometry in Pr$_2$NiMnO$_6$ material. The obtained n value is near 3/8, which indicates that the reaction rate-limiting step would be a process involving the charge transfer reaction.

Cathodic overpotential is an important parameter for SOFCs. Fig. 8 shows the typical curves of overpotential as a function of current density at different temperatures. It is observed that under the same current density, the cathodic overpotential decreases with the increase of measurement temperature. According to the Butler–Volmer equation, we can expect a linear expression at low overpotential (less than 20 mV), $i = i_0ZF\eta/R$, where $i$ is the current density, $i_0$ the exchange-current density, $\eta$ the overpotential, $F$ is the Faraday constant and $R$ is the universal gas constant. From the inverse of the derivative of $i$ against $\eta$, the polarization resistance can be calculated. The value obtained at 700 °C is 0.41 Ω cm$^2$, which is quite in agreement with the result obtained from the impedance measurement (Fig. 6). When the current density reaches 102 mA cm$^{-2}$ at 700 °C in air, the cathode overpotential is only 37 mV, comparable to the result of SrFe$_{0.7}$Cu$_{0.3}$O$_{3-\delta}$ material [43]. Therefore Pr$_2$NiMnO$_6$ can be
considered as a promising cathode candidate for IT-SOFCs, given that the electrode performance be further improved by optimizing the microstructure and/or forming composite cathodes.

Conclusions

The double perovskite material Pr$_2$NiMnO$_6$ has been proved as a potential cathode for IT-SOFCs, due to its high chemical stability, comparable thermal expansion behavior with the CGO electrolyte, and the promising electrochemical performance around 700 °C in air. Although the electric conductivity of Pr$_2$NiMnO$_6$ is quite low (approximately 3 S cm$^{-1}$ at 800 °C), the cathode performance is expected to be further improved by the optimization of the electrode microstructure and/or formation of composite electrode.

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