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Preparation of ReNiO_3 (Re = Pr, Sm, Eu) and proton conductivity

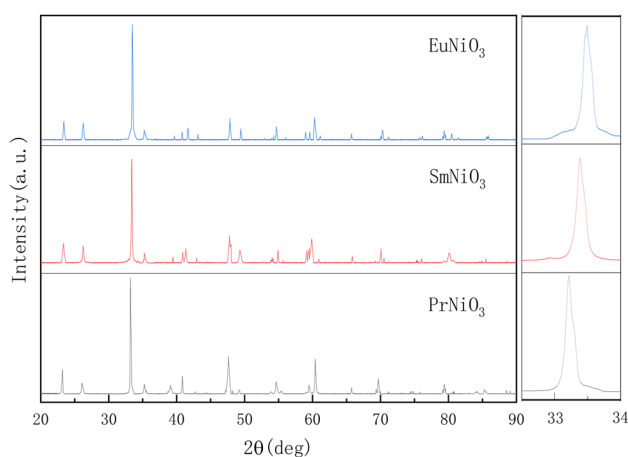
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ReNiO_3 (Re = Pr, Sm, Eu) solid electrolytes were prepared by the sol–gel method, which were sintered in a pure oxygen atmosphere of 20 MPa at 1000 °C for 24 hours. The DC resistivities of the three materials in air and in a hydrogen-containing atmosphere were tested respectively. The resistivities in the hydrogen-containing atmosphere were about 10^2 , 10^4 , and 10^5 times higher than those in air and XPS analysis showed that after 10% H_2 –Ar treatment, the proportion of Ni^{2+} of PrNiO_3 , SmNiO_3 and EuNiO_3 increased successively. The proton transport number of PrNiO_3 was lower than 0.5 at 50–500 °C, and SmNiO_3 and EuNiO_3 were almost pure proton conductors below 200 °C. The conductivities of SmNiO_3 and EuNiO_3 were $1.08 \times 10^{-4} \text{ S cm}^{-1}$ and $1.83 \times 10^{-5} \text{ S cm}^{-1}$ at 200 °C in 5% H_2 –Ar. The hydrogen sensing properties of SmNiO_3 and EuNiO_3 show that the measurement results of the two materials were accurate in the range of 0.5–10% H_2 .

1. Introduction

Proton conductors have always been a focus and research object for fuel cells,^{1–3} hydrogen sensors,^{4,5} and electrochemical hydrogen separation.^{6–8} In any field, researchers want materials with high proton conductivity and proton transport number. It is generally accepted that in order to obtain a higher proton conductivity, a higher proton concentration and a lower proton conduction barrier are required in the material.^{9,10} Theoretically, the concentration of oxygen ion vacancies determines the upper limit of proton concentration, so a large dose of dopant is required to produce a high concentration of oxygen ion vacancies, but too high a concentration of dopant may lead to poor stability of the material or the formation of other impurity phases. This indicates that typical perovskite proton conductors such as Y-doped BaCeO_3 and BaZrO_3 cannot increase proton concentration without limit by high dose doping. K. D. Kreuer¹¹ proposed that protons in ABO_3 perovskite materials with a tetravalent B-site (IV) have a lower transport barrier than in materials with a pentavalent B-site (V). Moreover, the trivalent B-site materials may have higher ionic conductivity. Therefore, some scholars have turned their attention to A(III)–B(III) type materials. Zhou *et al.*¹² first reported that protons can spontaneously bind to SmNiO_3 , the concentration of protons in SmNiO_3 may not be limited by the concentration of oxygen vacancies, and high proton conductivity can be obtained in a hydrogen-containing atmosphere at a lower temperature,

which has attracted wide attention. SmNiO_3 has a perovskite structure; due to its high electronic conductivity,^{13,14} it was not paid much attention at first. However, in a hydrogen-containing atmosphere, the material produces a Mott transition due to the inclusion of hydrogen, which inhibits the conduction of electrons,^{15,16} which is extremely favorable for enhancing the proton transport of the material. Moreover, the BO_6 octahedron in SmNiO_3 is conducive to proton conduction. At present, SmNiO_3 materials are generally prepared as thin films by vapor deposition or pulsed laser deposition.^{12,17,18} In fact, the thin films are affected by the substrate and the thickness of the film,^{19,20} and there are deficiencies in the area, uniformity, and repeatability of the films. Therefore, comparison of the different properties of rare earth nickelates would obviously require preparing the material into bulk samples by a conventional sintering method.


 Fig. 1 XRD patterns of ReNiO_3 (Re = Pr, Sm, Eu).

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2. Experiment

2.1 Preparation of ReNiO_3

To obtain metastable Ni^{3+} , high pressure sintering in pure oxygen is required.^{13,14,21} ReNiO_3 (Re = Pr, Sm, Eu) were prepared by the sol-gel method, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Aladdin), $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Aladdin), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Aladdin), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.99%, Aladdin) were accurately weighed according to the ratio and dissolved in water respectively, and the solution temperature was set at 80 °C.

Table 1 Crystal data of ReNiO_3 (Re = Pr, Sm, Eu)

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Unit cell volume (Å ³)
PrNiO ₃	5.4132	5.3828	7.6226	222.11
SmNiO ₃	5.4252	5.3373	7.5741	219.32
EuNiO ₃	5.4562	5.2938	7.5359	217.68

EDTA (AR, Aladdin) and citric acid monohydrate (AR, Aladdin) were used as complexing agents, EDTA : citric acid : metal ion = 1 : 1 : 1 (molar ratio). The pH of the solution was adjusted by HNO_3 and $\text{NH}_3 \cdot \text{H}_2\text{O}$ to keep it between 6 and 8. As the complexing reaction proceeds, the water evaporates continuously. When the gel was formed, it was transferred to the crucible and heated until the gel was dried to powder. The powder was ground and calcined in pure oxygen at 600 °C for 10 hours to obtain the brown-black precursor powder. The precursor powder was pressed into 10 mm diameter slices by cold isostatic pressure, and then sintered in pure oxygen atmosphere at 20 MPa and 1000 °C for 24 hours (the samples were kept in pure oxygen until cooled to room temperature) to obtain dense ceramic electrolytes.

After XRD (Smart Lab 9 kW) confirmation, the XRD of the three samples is consistent with the patterns of ReNiO_3 (Re = Pr, Sm, Eu) orthorhombic phases in the database (space group *Phm* (No. 62), ICDD reference number 01-079-2453, 01-080-1946, 01-085-2249), indicating that ReNiO_3 (Re = Pr, Sm, Eu)

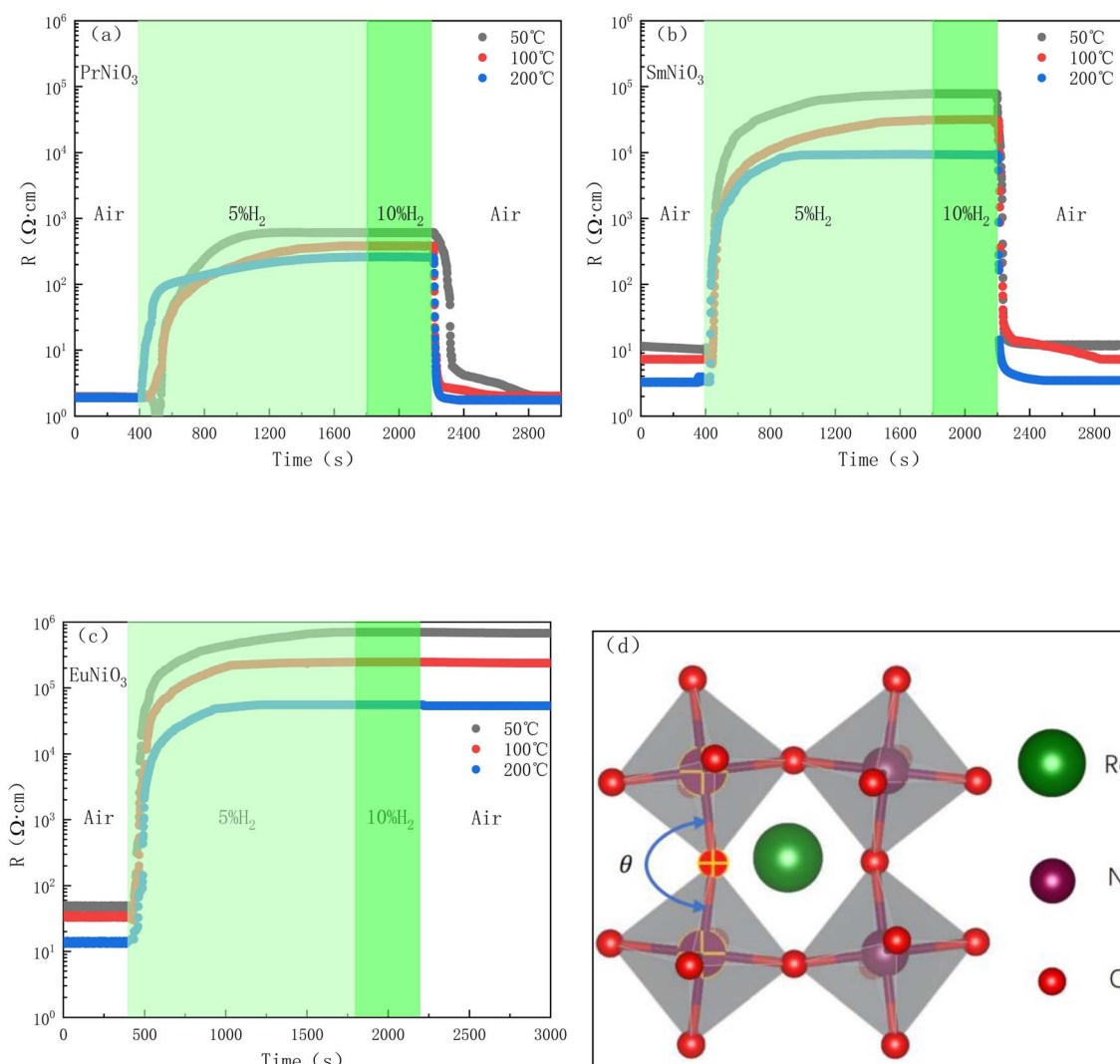


Fig. 2 DC resistivities of three materials in different atmospheres and schematic diagram of crystal structure (a) PrNiO_3 (b) SmNiO_3 (c) EuNiO_3 (d) schematic diagram of ReNiO_3 crystal structure.



has been successfully synthesized. Fig. 1 shows the XRD patterns of ReNiO_3 (Re = Pr, Sm, Eu) electrolyte.

Since the ionic radius $r(\text{Pr}^{3+}) > r(\text{Sm}^{3+}) > r(\text{Eu}^{3+})$, it can be seen from the local magnification of the main peak that the angle of the diffraction peak gradually shifts to the right. The crystal data after refining are listed in the following table (Table 1):

3. Results and discussion

3.1 DC resistivity of ReNiO_3 in different atmospheres

Fig. 2(a–c) show the DC resistivities of PrNiO_3 , SmNiO_3 and EuNiO_3 in air and hydrogen-containing atmosphere (measured by Keithley 2450, DC voltage is 100 mV, Pt was used as electrode material at two ends of electrolyte).

As shown in Fig. 2, the resistivities of the three materials are low in the air atmosphere for the first 400 s. This is due to the three materials are conductors or semiconductors with very low resistivity in the air,^{13,22} and the resistivities increase rapidly after the introduction of 5% H_2 -Ar. After the resistivities reaches

a constant value, the resistivities do not increase even if the concentration of hydrogen increases (~ 1800 s), and the time to reach equilibrium is shorter as the temperature increases and the resistivities of PrNiO_3 , SmNiO_3 and EuNiO_3 increases by about 10^2 , 10^4 and 10^5 times. When air is introduced at 2200 s, the resistivities of PrNiO_3 and SmNiO_3 decrease rapidly, and return to the initial resistivities in air around 300–400 s, while the resistivity of EuNiO_3 is almost unchanged after air introduction (since EuNiO_3 cannot recover the resistivity, Fig. 2(c) shows the measured curves of three EuNiO_3 samples of the same size). This is probably due to the reduction of tolerance factor t as the ion radius of Re^{3+} decreases ($t(\text{PrNiO}_3) = 0.925$, $t(\text{SmNiO}_3) = 0.894$, $t(\text{EuNiO}_3) = 0.887$),^{21,23} which makes the crystal structure deviate more from the perfect cubic phase ($t = 1$). The bond angle θ of Ni–O–Ni becomes smaller (as shown in Fig. 2(d)), and the valence of Ni^{3+} becomes more and more unstable²⁴ and becomes more and more responsive to hydrogen.

Fig. 3 shows the XPS (Thermo Scientific K-Alpha) of the three samples before and after 10% H_2 -Ar treatment. As shown in

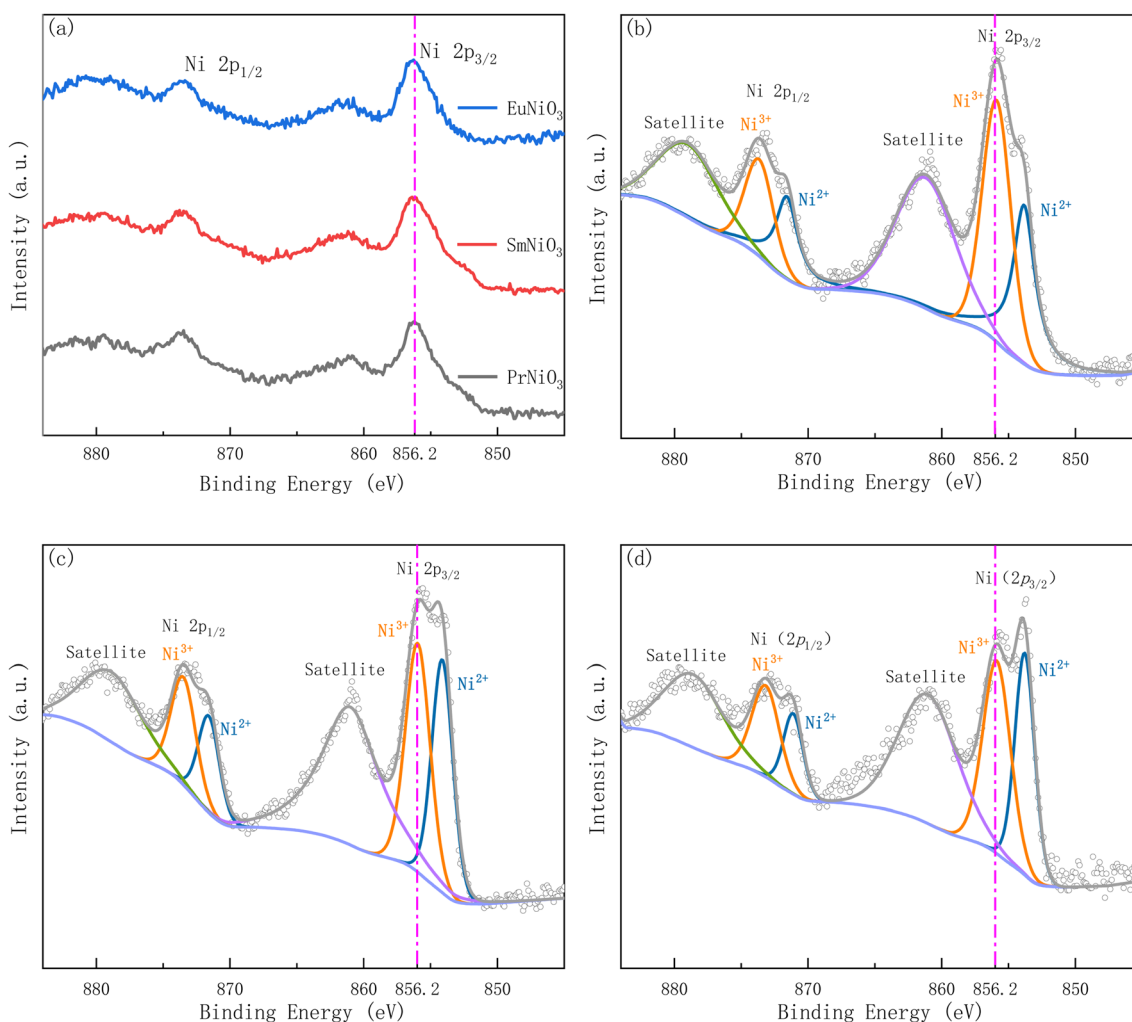


Fig. 3 XPS spectra of three samples before and after 10% H_2 -Ar treatment (a) ReNiO_3 (Re = Pr, Sm, Eu) before hydrogen treatment (b) PrNiO_3 after hydrogen treatment (c) SmNiO_3 after hydrogen treatment (d) EuNiO_3 after hydrogen treatment.



Fig. 3(a) that the Ni(2p_{3/2}) peaks of the three samples before 10%H₂-Ar treatment are all at the position of 852.2 eV binding energy. The peak at this location is assigned to Ni³⁺.^{25,26} However, after 10%H₂-Ar treatment (the samples were stabilized in 10%H₂-Ar for 1 hour at 50 °C), the peak of Ni(2p_{3/2}) shifted significantly towards the direction of low binding energy, as shown in Fig. 3(b-d), indicating that the average valence state of Ni element decreased. Moreover, after peak-differentiating and imitating of the XPS spectra of the three samples treated with 10%H₂-Ar, it is found that the peak intensity of the Ni²⁺ in PrNiO₃, SmNiO₃ and EuNiO₃ gradually increases, indicating that the proportion of Ni²⁺ is increasing, which is consistent with the trend of increasing resistivity ratio of the three samples in hydrogen and air.

However, this cannot fully explain that EuNiO₃ is irreversible. Some scholars believe that hydrogen insertion will reduce the Gibbs free energy of the system.²⁷ The smaller ion radius of Re³⁺ is, the easier the process of hydrogen insertion will be until EuNiO₃ becomes spontaneous reaction. However, this computing method²⁸ is the inference which is based on A-site = La, B-site = Fe, Co, Mn elements, and assumes that the oxides in the system are immiscible, which may deviate from the reality.

3.2 Measurement of proton transport number

The proton transport number was measured by electromotive force method (Aremco 503 ceramic bond is used as sealant between electrolyte and fixture). According to the formula,

$$E = \frac{RT}{2F} \ln \left(\frac{pH'_2}{pH''_2} \right)$$

E is electromotive force; R is the ideal gas constant, 8.314 J (mol K)⁻¹; F is Faraday's constant, 96485 C mol⁻¹; pH'₂ is 4%H₂-Ar; pH''₂ is 2%H₂-Ar.

Therefore, proton transport number(t_H) is the actual electromotive force (E_{act}) ratio of the theoretical electromotive force (E_{th}).

Fig. 4(a) shows E_{th} and E_{act} of the ReNiO₃, and Fig. 4(b) shows the proton transport number of the ReNiO₃.

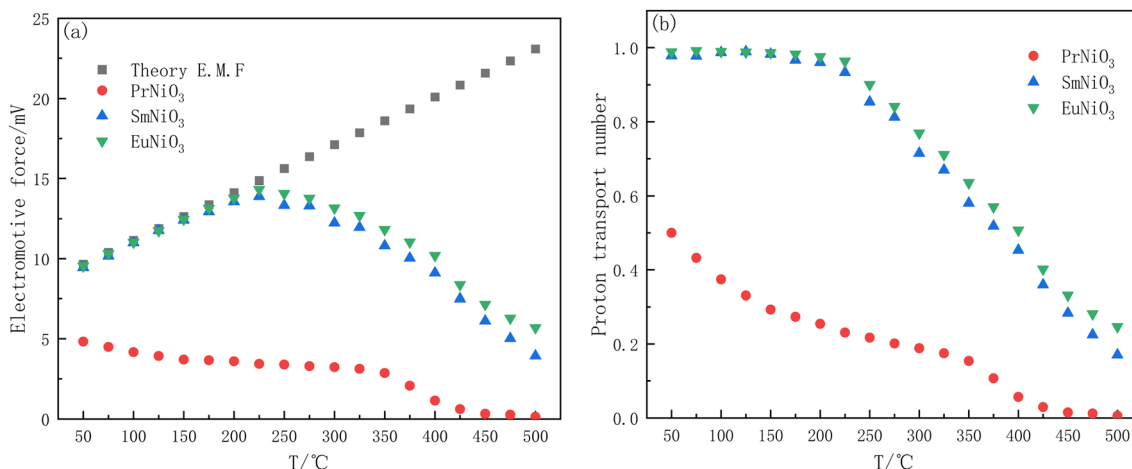


Fig. 4 The EMF (a) and proton transport number (b) of the ReNiO₃.

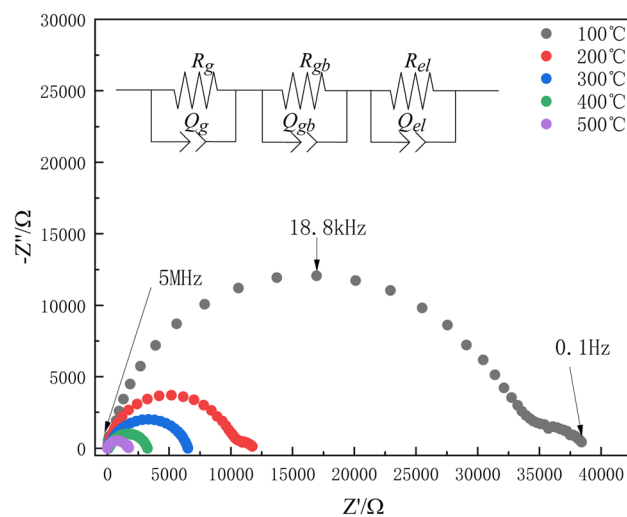


Fig. 5 Partial impedance spectra of SmNiO₃ in 5%H₂-Ar.

Table 2 The relation between conductivity and temperature of SmNiO₃ and EuNiO₃ (50–200 °C)

Materials	Pre-exponential factor (line intercept)	E_a /eV
SmNiO ₃	2.445	0.220
EuNiO ₃	1.605	0.259

As shown in Fig. 4(b) that the proton transport number of PrNiO₃ is low and always less than 0.5, indicating that proton is not the main carrier in PrNiO₃ and cannot be used as

Table 3 The relation between conductivity and temperature of SmNiO₃ and EuNiO₃ (400–500 °C)

Materials	Pre-exponential factor (line intercept)	E_a /eV
SmNiO ₃	4.398	0.332
EuNiO ₃	4.668	0.417



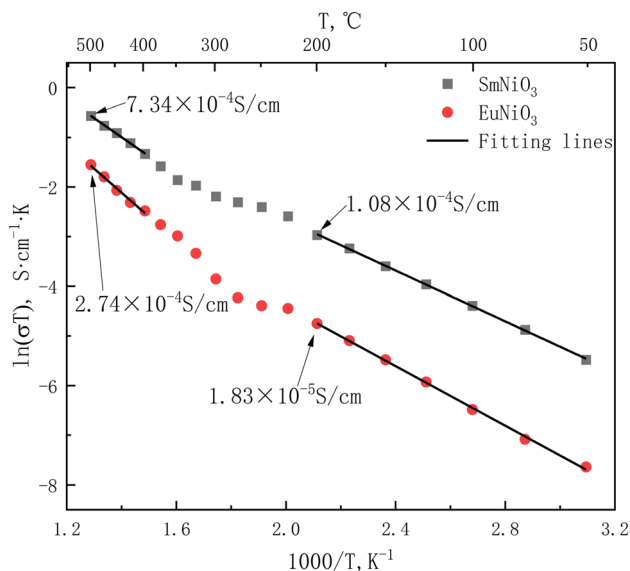


Fig. 6 Arrhenius curves of SmNiO_3 and EuNiO_3 .

a proton conductor. When the temperature exceeds $400\text{ }^\circ\text{C}$, the actual electromotive force of PrNiO_3 is almost 0, and the electrolyte is in the state of short circuit. The E_{act} of SmNiO_3

and EuNiO_3 is very close to the E_{th} below $225\text{ }^\circ\text{C}$, and the two materials are almost pure proton conductors. The proton transport number decreases with increasing temperature, and the proton transport number of EuNiO_3 is slightly higher than that of SmNiO_3 .

3.3 Measurement of electrical conductivity

After the SmNiO_3 and EuNiO_3 were stabilized in $5\%\text{H}_2\text{-Ar}$ at $50\text{ }^\circ\text{C}$ for 30 min, the conductivities of the two samples were measured by AC impedance (Solartron 1260). The frequency range is $5 \times 10^6\text{-}10^{-1}\text{ Hz}$, and the AC voltage is 100 mV.

Fig. 5 shows part of the AC impedance spectrum of SmNiO_3 in $5\%\text{H}_2\text{-Ar}$. The circuit in the figure is used for impedance fitting (R_b represents bulk resistance, R_{gb} represents grain boundary resistance, R_{el} represents resistance of interface or electrode process).

According to AC impedance at different temperatures, the electrical conductivities and activation energy (E_a) of the materials were calculated and listed in Tables 2 and 3 and Arrhenius curve are showed in Fig. 6.

Compared with the films prepared by RF magnetron sputtering¹² and pulsed laser deposition,¹⁷ the conductivity of the materials prepared by solid-phase sintering method is about 2 orders of magnitude lower, but the activation energy is slightly

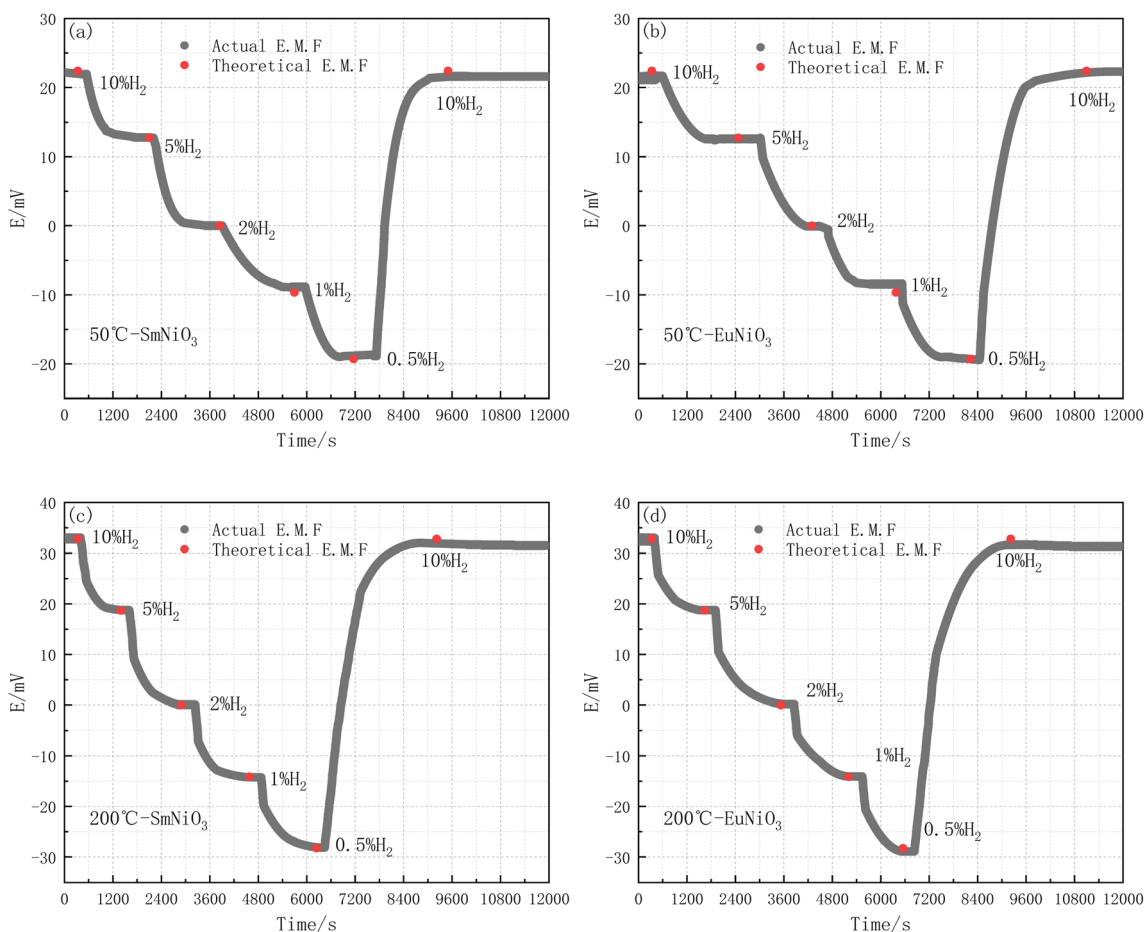


Fig. 7 Hydrogen sensing properties of SmNiO_3 and EuNiO_3 (a) $50\text{ }^\circ\text{C-SmNiO}_3$ (b) $50\text{ }^\circ\text{C-EuNiO}_3$ (c) $200\text{ }^\circ\text{C-SmNiO}_3$ (d) $200\text{ }^\circ\text{C-EuNiO}_3$.



lower than that of the films (0.23–0.37 eV),¹⁷ indicating that the materials are more likely to transport protons without the influence of substrate.

3.4 Hydrogen sensing properties of SmNiO₃ and EuNiO₃

After the SmNiO₃ and EuNiO₃ electrolyte tablets were stabilized in 2%H₂-Ar for 30 min, the sensing properties of SmNiO₃ and EuNiO₃ at 50 °C and 200 °C were tested by using 2%H₂-Ar as a reference gas.

As shown in Fig. 7 that the actual EMF of SmNiO₃ and EuNiO₃ at different hydrogen partial pressures of 50 °C and 200 °C is very close to the theoretical EMF. The time from response to equilibrium for SmNiO₃ and EuNiO₃ at 50 °C is approximately 1800 s, and the time at 200 °C is approximately 1500 s.

4. Conclusion

ReNiO₃ (Re = Pr, Sm, Eu) were prepared by the sol-gel method. The sintering conditions were as follows: pure oxygen atmosphere of 20 MPa, sintering at 1000 °C for 24 hours. The DC resistivities of ReNiO₃ (Re = Pr, Sm, Eu) in a hydrogen-containing atmosphere are about 10², 10⁴, and 10⁵ times higher than in air. XPS analysis shows that after hydrogen treatment, the proportion of Ni²⁺ in PrNiO₃, SmNiO₃ and EuNiO₃ increased successively, which was consistent with the trend of increasing resistivity ratio. The electromotive force method was used to measure the proton transport number of the three materials. The results show that the proton transport number (t_{H}) of PrNiO₃ is always lower than 0.5 in the test temperature range, and almost 0 when the temperature is higher than 400 °C. SmNiO₃ and EuNiO₃ are almost pure proton conductors below 200 °C, and the proton transport number decreases gradually with the increasing temperature. The conductivities of SmNiO₃ and EuNiO₃ are measured by AC impedance in 5%H₂-Ar. The results show that the conductivities of SmNiO₃ and EuNiO₃ are 1.08×10^{-4} S cm⁻¹ and 1.83×10^{-5} S cm⁻¹ at 200 °C. The conductivities are 7.34×10^{-4} S cm⁻¹ and 2.74×10^{-4} S cm⁻¹ at 500 °C. The activation energies (E_{a}) of SmNiO₃ are 0.220 eV (50–200 °C) and 0.332 eV (400–500 °C), and those of EuNiO₃ are 0.259 eV (50–200 °C) and 0.417 eV (400–500 °C). The hydrogen sensing properties of SmNiO₃ and EuNiO₃ show that the measurement results of both materials are accurate in the range of 0.5–10%H₂. The equilibrium time is about 1800 s at 50 °C and 1500 s at 200 °C.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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