J Mater Sci (2010) 45:5860–5864
DOI 10.1007/s10853-010-4662-6

Proton conduction at intermediate temperature and its application in ammonia synthesis at atmospheric pressure of $BaCe_{1-x}Ca_xO_{3-\alpha}$

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Received: 13 January 2010 / Accepted: 26 May 2010 / Published online: 22 June 2010

Abstract Dense ceramic samples of $BaCe_{1-x}Ca_xO_{3-\alpha}$ ($x = 0.05, 0.10, 0.15, 0.20$) have been synthesized by heat treating the precursor prepared from a microemulsion route under lower calcining and sintering temperatures than traditional high-temperature solid-state reaction. The samples exhibited single phase of orthorhombic perovskite. It was found that the samples were almost pure proton conductors in wet hydrogen at 300–600 °C. Ammonia was synthesized successfully from nitrogen and hydrogen gases at atmospheric pressure using $BaCe_{0.9}Ca_{0.1}O_{3-\alpha}$ as an electrolyte of ammonia synthesis reactor.

Introduction

$BaCeO_3$-based ceramic as a kind of proton-conducting functional material have attracted considerable attention due to their potential applications in hydrogen fuel cell, hydrogen sensor, steam electrolyzer, separation and purification of hydrogen, hydrogenation and dehydrogenation of some organic compounds and ammonia synthesis at atmospheric pressure, etc. [1–3]. When some trivalent or divalent metal cations partially substitute for Ce^{4+} site in $BaCeO_3$, oxygen vacancies, which play an important role in forming the protons in hydrogen- or water vapor-containing atmospheres, are formed due to charge compensation. Typically, dopant cations are trivalent rare earth metal ions and Ca^{2+} ion. In spite of usually lower proton conductivity compared to rare earth metal oxide-doped $BaCeO_3$, calcium oxide-doped $BaCeO_3$ still is interesting due to rich source and cheapness of calcium oxide. Iwahara et al. reported that $BaCe_{1-x}Ca_xO_{3-\alpha}$ exhibited an almost pure ionic conduction in wet hydrogen and a mixed ionic (protonic + oxide-ionic) conduction under hydrogen–air fuel cell condition at 600–1,000 °C [4]. Slade et al. reported that $BaCe_{1-x}Ca_xO_{3-\alpha}$ possessed the protonic conduction as confirmed by electromotive force (emf) measurements using the ceramics as the solid-electrolyte membranes separating moist and dry nitrogen at 400–800 °C [5–7]. However, the investigation on protonic conduction in $BaCe_{1-x}Ca_xO_{3-\alpha}$ at intermediate temperatures of 300–600 °C until now was still insufficient. In addition, the calcining and sintering temperatures for synthesis of $BaCe_{1-x}Ca_xO_{3-\alpha}$ by solid-state reaction were as high as 1,400 and 1,665 °C, respectively [4], and should be decreased to reduce the processing cost of devices based on $BaCe_{1-x}Ca_xO_{3-\alpha}$.

In this study, dense ceramic samples of $BaCe_{1-x}Ca_xO_{3-\alpha}$ were obtained by heat treating the precursor prepared from a microemulsion route under lower calcining and sintering temperatures than traditional high-temperature solid-state reaction. The proton-conducting behaviors of $BaCe_{1-x}Ca_xO_{3-\alpha}$ were investigated in the intermediate temperature range of 300–600 °C.

The traditional ammonia synthesis method is the Haber process, in which gaseous nitrogen and hydrogen react on catalyst under the temperatures of 430–480 °C, and especially under the high pressures of 15–30 MPa. Moreover the rate of H_2 conversion is low (10–15%) due to the thermodynamic limitations. In 1998, ammonia synthesis at

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atmospheric pressure has been realized successfully in an electrolytic cell reactor using a high-temperature proton conductor $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ [3]. The ammonia synthesis at atmospheric pressure in an electrolytic cell based on proton conductor has attracted a great attention. Since then, based on the pioneering work of Marnellos and Stoukides, considerable efforts have focused on various aspects of the cell reactor in order to improve the ammonia formation rate [8–20]. Stoukides research group has studied in detail the ammonia synthesis reaction in solid-state proton-conducting cells on Pd electrodes and on an industrial Fe catalyst by using strontia–ceria–ytterbia electrolyte [3, 9, 10]. More recently, they first demonstrated the feasibility of an electrocatalytic process in which ammonia was synthesis from steam and nitrogen by using either oxygen ion or proton-conducting solid-electrolyte cells [10]. Yiokari et al. have reported that the catalytic activity of industrial ammonia synthesis catalysts could be enhanced by up to 1300% by interfacing the catalyst with a $CaIn_{0.1}Zr_{0.9}O_{3-\alpha}$ proton conductor and electrochemically supplying protons to the catalyst surface [11]. Wherein, the effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA) was first demonstrated under high (50 bar) pressure. In addition, many other ion conductors such as $La_{1.9}Ca_{0.1}Zr_2O_{6.95}$ [12], $Ce_{0.2}M_{0.2}O_{2-\delta}$ (M = La, Y, Gd, Sm) [13], Ca^{2+}-doped $La_2M_2O_7$ (M = Ce, Zr) [14], $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ [15], $La_{0.9}M_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$ (M = Ca, Sr, Ba) [16, 17], $BaCe_{1-x}M_xO_{3-\alpha}$ [18] have been extensively studied as possible electrolytes for ammonia synthesis. Not long ago, Liu and his coworkers reported that high ammonia formation rate was obtained at atmospheric pressure and low temperature (25–100 °C) by using Ni–$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (Ni-SDC) as an anode, various cathode catalysts [$Sm_{1.5}Sr_{0.5}MO_4$ (M = Ni, Co, Fe), $SmFe_{0.7}Cu_{0.3-x}Ni_xO_3$ (x = 0, 0.1, 0.2, 0.3)], and Nafion proton exchange membrane as a proton permeating membrane [19, 20]. The highest rate of evolution of ammonia was up to 1.13×10^{-8} mol cm^{-2} s^{-1} using $SmFe_{0.7}Cu_{0.1}Ni_{0.2}O_3$ as the cathode at 80 °C [20]. In this study, we have successfully applied $BaCe_{0.9}Ca_{0.1}O_{3-\alpha}$ prepared via the microemulsion route to ammonia synthesis at atmospheric pressure.

Experimental

The precursors of $BaCe_{1-x}Ca_xO_{3-\alpha}$ (x = 0.05, 0.10, 0.15, 0.20) were prepared by a microemulsion route. The microemulsion A was prepared as follows. The required amounts of $Ba(C_2H_3O_2)_2$, $Ce(NO_3)_3{\cdot}6H_2O$, CaO reagents were dissolved by stirring in distilled water. Then the required amounts of cyclohexane (as the oil phase), alcohol (as the cosurfactant), and PEG (as the surfactant) were added by stirring into the above solution. The microemulsion B containing $(NH_4)_2CO_3$–NH_4OH (as the co-precipitating reagent), cyclohexane, alcohol, and PEG was prepared by the processes similar to the microemulsion A. Then, the microemulsion B was dripped into the microemulsion A under stirring. The formed white co-precipitate suspension was filtrated and dried. The as-obtained white co-precipitate precursor was calcined at 1,050 °C in air for 10 h. The oxides after calcining were milled with anhydrous ethanol by ball milling and dried, followed by sieving (100 mesh). The obtained ceramic powders were pressed into pellets by a hydrostatic pressure of 2.5×10^8 Pa and sintered at 1,500 °C for 12 h in air. The as-prepared ceramics were made into disks with thickness 0.6 mm and diameter 13 mm to serve as the electrolytes, and porous argent–palladium slurry was used as electrode material for the electrochemical determinations.

SEM (S-4700, HITACHI) was used to characterize the morphology of $BaCe_{1-x}Ca_xO_{3-\alpha}$ ceramics, and the phase structure was determined by powder X-ray diffraction (XRD) analysis (Rigaku D/MAX-IIIC X-ray diffractometer).

The conductivity was measured in wet hydrogen, H_2O–Ar and D_2O–Ar at 300–600 °C by an AC impedance method using electrochemical workstations (Zahner IM6EX) over the frequency range from 1 Hz to 3 MHz. In order to study the ionic conduction, the following hydrogen concentration cell was constructed using disk-shaped ceramic samples as solid electrolytes [21].

$$(+)\ \text{wet}\ H_2,\ Ag{-}Pd|BaCe_{1-x}Ca_xO_{3-\alpha}|Ag{-}Pd,\ \text{wet}\ H_2{-}Ar\ (p_{H_2})\ (-)$$

The partial pressure of hydrogen gas, p_{H_2}, in the H_2–Ar mixed gas was controlled by mixing argon and hydrogen gases in a given ratio.

In order to verify the proton conduction in these samples directly, the electrochemical hydrogen permeation (hydrogen pumping) [22] through the samples was performed by sending a direct current to the following electrolytic cell:

$$(+)\ \text{wet}\ H_2,\ Ag{-}Pd|BaCe_{1-x}Ca_xO_{3-\alpha}|Ag{-}Pd,\ \text{dry Ar}\ (-)$$

High pure hydrogen (99.999%) was saturated water vapor at given temperature and supplied to the anode chamber. The high pure argon (99.999%) was dried using a cold trap based on low temperature nitrogen gas (about −120 °C) and passed through the cathode chamber to carry the generated hydrogen gas to a gas chromatograph (Kexiao, GC1600), therein the amount of hydrogen gas generated was determined.

The electrolytic cell for ammonia synthesis at atmospheric pressure was constructed:

$$(+)\ \text{wet}\ H_2,\ Ag{-}Pd|BaCe_{0.9}Ca_{0.1}O_{3-\alpha}|Ag{-}Pd,\ \text{dry}\ N_2\ (-)$$

The Ag–Pd paste (weight percent: 20% Pd) was painted on two surfaces dried by infrared lamp and then fired at

900 °C for 20 min as current collectors and catalysts. The superficial surface area of each electrode was 0.5 cm^2 and the true catalytic surface area of each electrode was about 30 cm^2. In the ammonia synthesis experiments, the cathode and anode were filled with dry high pure nitrogen stream (99.999%, dried by a cold trap based on liquid nitrogen) and a high pure hydrogen stream (99.999%, $p\mathrm{H_2O} = 0.023$ atm), respectively. The flow rate of the two gases was 30 mL/min. When a direct current was sent to the electrolytic cell, $\mathrm{H_2}$ turned into protons by losing electrons on interface between the anode and the electrolyte, and permeated through the sample to the interface between the cathode and the electrolyte, therein protons reacted with $\mathrm{N_2}$ and formed $\mathrm{NH_3}$, as expressed by the following reactions:

Anode: $3\mathrm{H_2} \rightarrow 6\mathrm{H^+} + 6\mathrm{e^-}$

Cathode: $\mathrm{N_2} + 6\mathrm{H^+} + 6\mathrm{e^-} \rightarrow 2\mathrm{NH_3}$

The formed $\mathrm{NH_3}$ was absorbed by diluted sulfuric acid, and then the concentration of $\mathrm{NH_4}^+$ was analyzed by spectrophotometry [16]. The blank test was also performed under open circuit condition.

Results and discussion

Figure 1a, b shows that the XRD patterns of $\mathrm{BaCe}_{1-x}\mathrm{Ca}_x\mathrm{O}_{3-\alpha}$ calcined at 1,050 °C for 10 h and sintered at 1,500 °C for 12 h, respectively. There was a small peak near the position 50° from the Fig. 1a of the sample calcined at 1,050 °C for 10 h with highest content of Ca. From the Fig. 1b, we also found that the small peak disappeared after sintering at 1,500 °C for 12 h, indicating that all the samples prepared by microemulsion route have formed a single phase of $\mathrm{BaCeO_3}$ orthorhombic perovskite. There were not visible pores allowed gas molecules permeating as confirmed by scanning electron microscope (SEM) images. The densities of the ceramic samples were higher than 95% of the theoretical. The calcining and sintering temperatures were reduced by 350 and 165 °C, compared with those (1,400 and 1,665 °C) of traditional solid-state reaction [4], respectively. Transmission electron microscopy (TEM) images of the precursors of $\mathrm{BaCe}_{1-x}\mathrm{Ca}_x\mathrm{O}_{3-\alpha}$ prepared from the microemulsion route displayed that the precursor particles appeared to be spherical in a narrow size distribution range of about 20–30 nm and without serious agglomeration. This is because in the mixed microemulsion system the well-dispersed aqueous droplets in the oil phase can act as micro-reactors, and a co-precipitation reaction occurred only within the droplets, thus resulting in the formation of uniform spherical co-precipitate particles with high homogeneous in the chemical composition [18, 23]. Therefore, as compared to the solid-state reaction route [4], the microemulsion route in this study is no doubt favorable for reducing the calcining and sintering temperatures of the precursor powders.

As shown in Fig. 2a, the conductivities of $\mathrm{BaCe_{0.9}Ca_{0.1}O_{3-\alpha}}$ in wet hydrogen increased in the order: σ $(x = 0.05) < \sigma$ $(x = 0.20) < \sigma$ $(x = 0.15) < \sigma$ $(x = 0.10)$. The maximum conductivity was observed to be 7.64×10^{-4} S cm^{-1} for $x = 0.10$ at 600 °C. It may be interpreted by the following defect chemistry:

$$\mathrm{CaO} \xrightarrow{\mathrm{BaCeO_3}} \mathrm{Ca}_{\mathrm{Ce}}'' + \mathrm{V}_{\mathrm{O}}^{\bullet\bullet} + 3\mathrm{O}_{\mathrm{O}}^{\times} \tag{1}$$

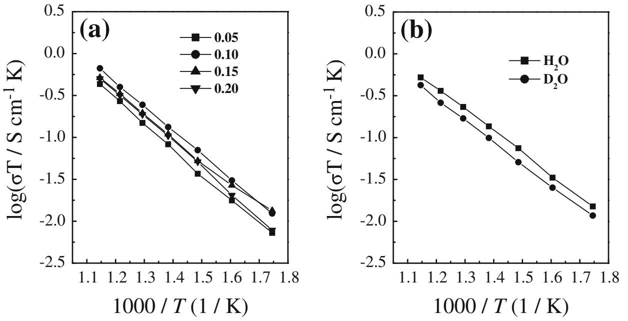
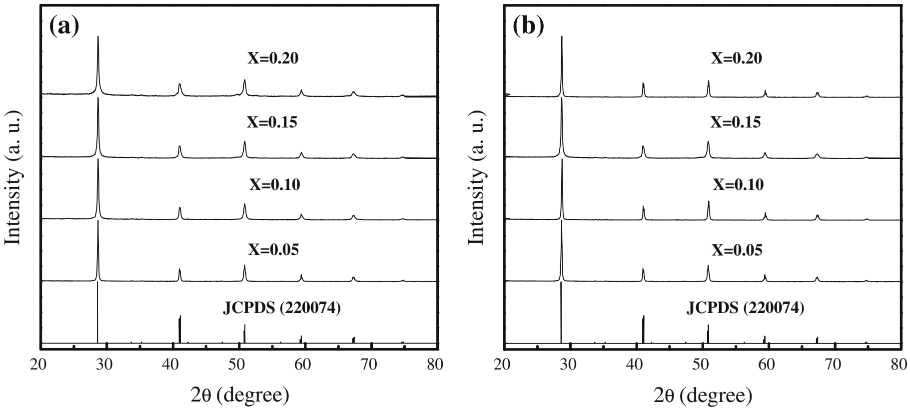


Fig. 2 Conductivities of **a** $\mathrm{BaCe}_{1-x}\mathrm{Ca}_x\mathrm{O}_{3-\alpha}$ in wet hydrogen and **b** $\mathrm{BaCe_{0.9}Ca_{0.1}O_{3-\alpha}}$ in $\mathrm{H_2O}$–Ar (Ar saturated with water vapor at 20 °C) and $\mathrm{D_2O}$–Ar (Ar saturated with heavy water vapor at 20 °C) at 300–600 °C

Fig. 1 Powder X-ray diffraction of $\mathrm{BaCe}_{1-x}\mathrm{Ca}_x\mathrm{O}_{3-\alpha}$ **a** calcined at 1,050 °C in air for 10 h and **b** sintered at 1,500 °C in air for 12 h



It can be seen from reaction (1) that the effective concentration (or activity) of oxygen vacancy of $BaCe_{1-x}Ca_xO_{3-\alpha}$ may increase with increasing the doping level. However, on the other hand, the concentrations of the point defect pairs $\left(V_O^{\bullet\bullet}Ca''_{Ce}\right)$ and $\left(Ca''_{Ce}\,V_O^{\bullet\bullet}\,Ca''_{Ce}\right)$, which result from the coulombic attraction between $V_O^{\bullet\bullet}$ and Ca''_{Ce}, may also increase with increasing the doping level, resulting in decrease in the effective oxygen vacancy concentration. The two opposite effects may result in the highest effective oxygen vacancy concentration and then the highest conductivity for $x = 0.10$.

Figure 2b shows an isotope effect on the conductivity of $x = 0.10$ in H_2O–Ar (Ar saturated with water vapor at 20 °C) and in D_2O–Ar (Ar saturated with heavy water vapor at 20 °C) at 300–600 °C. The ratio of the pre-exponential factor, A_D/A_H, was equal to 1.21, which was close to $1 < A_D/A_H < \sqrt{2}$ [24], indicating that the samples possessed protonic conduction in water vapor-containing atmosphere. The similar results were also observed for the other samples in this study.

In order to investigate the ionic conduction in $BaCe_{1-x}Ca_xO_{3-\alpha}$, hydrogen concentration cells using $BaCe_{1-x}Ca_xO_{3-\alpha}$ as electrolytes were constructed. According to the reports by Shimura [25] and Ma [26], the ionic (proton + oxide ion) transport number (t_i) in hydrogen atmosphere may be estimated by comparing the observed emf value (E_{obs}) of the hydrogen concentration cell with the corresponding theoretical values (E_{cal}) calculated from the Nernst equation.

$$E = \frac{RT}{2F}\ln\frac{p_{H_2(I)}}{p_{H_2(II)}} \tag{2}$$

Figure 3a shows emf results of the representative sample. It is evident that the each observed value was close to the corresponding theoretical value. The ionic transport number t_i ($=E_{obs}/E_{cal}$) was unity at 400–600 °C, indicating that the conductivity in hydrogen atmosphere as shown in Fig. 2a was pure ionic.

Figure 3b shows the results of the electrochemical hydrogen permeation (hydrogen pumping) using $BaCe_{0.9}Ca_{0.1}O_{3-\alpha}$ as an electrolyte. The dotted line shows the theoretical value, which is calculated based on Faraday's law and the assumption that the charge carriers in these ceramics are only protons. As shown in Fig. 3b, when the current density was <16 mA cm^{-2}, the hydrogen evolution rate was close to the theoretical value, the proton transport number $t_H^+ \approx 1$, indicating that the sample was almost a pure proton conductor under hydrogen atmosphere. When the current density was higher than 16 mA cm^{-2}, the hydrogen evolution rate deviated from the theoretical value. It may be relevant to some electronic conductivity created from the polarization under larger current density conductions [26].

The ammonia was synthesized in an electrolytic cell using $BaCe_{0.9}Ca_{0.1}O_{3-\alpha}$ with the highest proton conductivity as an electrolyte. The blank test under open circuit conditions (imposed current was zero) demonstrated no detectable ammonia under these conditions. Figure 4a shows the relationship between the rate of ammonia formation and the reaction temperature under a direct current of 1 mA. It can be seen that the rate of ammonia synthesis first increased as increasing temperature up to 480 °C, and then decreased. The maximum rate of ammonia formation appeared at 480 °C which was the optimum temperature for the ammonia synthesis in this study. Figure 4b shows the relationship between the rate of ammonia formation and the applied current at 480 °C. The rate of ammonia formation increased with increasing applied current, then was almost invariable after 0.8 mA. It may be considered that 0.8 mA was the optimum current for ammonia synthesis in this study. It was found that the current of 0.8 mA sent to the electrolytic cell was almost equal to protonic current through the sample, which was limited by the

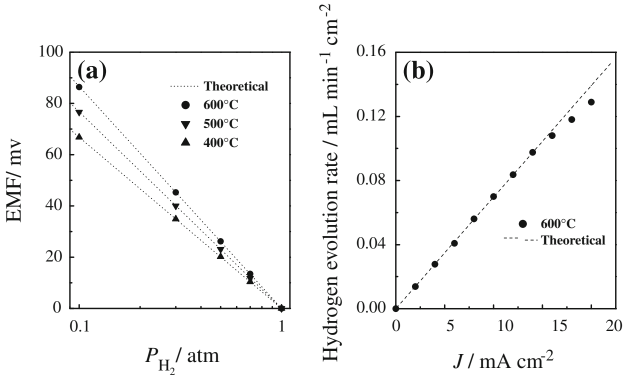


Fig. 3 **a** EMF of the hydrogen concentration cell: wet H_2, Ag–Pd|$BaCe_{0.9}Ca_{0.1}O_{3-\alpha}$|Ag–Pd, wet H_2-Ar $\left(p_{H_2}\right)$. The *lines* show the theoretical EMF at each temperature. **b** Electrochemical hydrogen permeation (hydrogen pumping) rate using $BaCe_{0.9}Ca_{0.1}O_{3-\alpha}$ as an electrolyte. The operating temperature was 600 °C

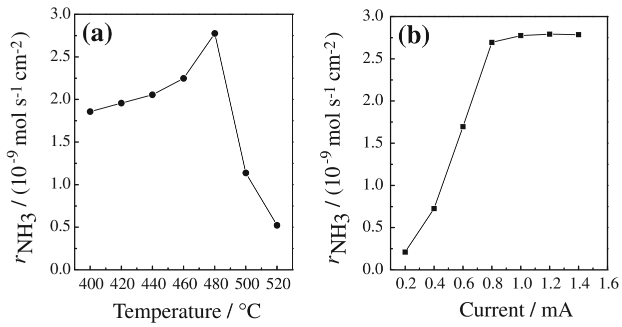


Fig. 4 **a** The relationship between the rate of ammonia formation and operating temperature for the electrolytic cell using $BaCe_{0.9}Ca_{0.1}O_{3-\alpha}$ as an electrolyte under a direct current of 1 mA. **b** The relationship between the rate of ammonia formation and the applied current for the electrolytic cell using $BaCe_{0.9}Ca_{0.1}O_{3-\alpha}$ as an electrolyte at 480 °C

protonic conductivity at 480 °C. If the current is above 0.8 mA, an electronic conduction in the sample may be produced, thereby the current efficiency for the NH_3 formation may be reduced [23]. The maximum rate of NH_3 formation and the percent conversion (i.e., the current efficiency) of the electrochemically supplied H_2 were 2.69×10^{-9} mol s^{-1} cm^{-2} and ca. 50%, respectively, under a direct current of 0.8 mA at 480 °C.

Conclusions

$BaCe_{1-x}Ca_xO_{3-\alpha}$ ($x = 0.05$, 0.10, 0.15, 0.20) ceramic samples were prepared via a microemulsion route. The calcining and sintering temperatures were lowered by 350 and 165 °C than those of traditional high-temperature solid-state reaction, respectively. This may be related to the favorable dispersion, high homogeneous in the chemical composition, ultrafine size of powders prepared via a microemulsion route. The ceramic samples were almost pure proton conductors in wet hydrogen, the protonic conductivities increased in the order: σ ($x = 0.05$) < σ ($x = 0.20$) < σ ($x = 0.15$) < σ ($x = 0.10$) at 300–600 °C. The maximum protonic conductivity was observed to be 7.64×10^{-4} S cm^{-1} for $x = 0.10$ at 600 °C. Ammonia was synthesized successfully at atmospheric pressure in an electrolytic cell using $BaCe_{0.9}Ca_{0.1}O_{3-\alpha}$ as electrolyte. The optimum current applied and operating temperature for ammonia synthesis at atmospheric pressure in this study were 0.8 mA and 480 °C, respectively. The maximum ammonia formation rate and the percent conversion (i.e., the current efficiency) of the electrochemically supplied H_2 were 2.69×10^{-9} mol s^{-1} cm^{-2} and about 50%, respectively, under a direct current of 0.8 mA at 480 °C.

Acknowledgement This work was supported by the National Natural Science Foundation of China (No. 20771079).

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