

Short communication

Unique porous thick $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ solid oxide fuel cell cathode films prepared by spray pyrolysis

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Abstract

Ultrasonic spray pyrolysis assisted by an electrostatic field was used to deposit thick $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC) films ($>40\ \mu\text{m}$) as solid oxide fuel cell (SOFC) cathodes with a unique porous columnar structure. The high porosity and great thickness provided many active sites for reduction reaction. The space between columns, as well as the large pores ($\sim 100\ \text{nm}$) inside the columns allowed gas molecules to diffuse quickly to the reaction sites; thus, very low interfacial resistance values (0.20 and $0.035\ \Omega\ \text{cm}^2$ at 600 and $700\ ^\circ\text{C}$, respectively) were obtained. Moreover, the high deposition rate, ease of operation in open air and low cost make the ultrasonic spray pyrolysis assisted by an electrostatic field a particularly useful method for preparation of films ideal for SOFC operation.

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Keywords: Solid oxide fuel cell; $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$; Cathode; Spray pyrolysis

1. Introduction

Solid oxide fuel cells (SOFCs) have experienced phenomenal progress in the last two decades because of their promise of higher efficiencies and lower pollutant emissions in comparison to fossil fuel-based energy sources [1,2].

Although conventional solid-state reaction routes are indispensable for large cells and mass production, the ball-milling and repeated grinding and sintering required are energy-intensive and time-consuming. In addition, the composition homogeneity in the resultant powder is often unsatisfactory. Moreover, subsequent steps such as slurry coating, tape casting or screen-printing and co-firing with the electrolyte further increase the overall complexity and cost for the manufacturing of SOFCs. In pursuit of a simple one-step solution, a variety of vapor processing techniques have been used to fabricate the electrode films of SOFCs, such as chemical vapor deposition [3], physical vapor deposition [4], and electrochemical vapor deposition

[5,6]. These vapor processing methods are generally very expensive because sophisticated reactors and/or vacuum systems are required. Therefore, a cost-effective film deposition method that can be operated in open air is highly desirable. Spray pyrolysis is such a method and is often employed to prepare thin dense transparent conducting films [7] and thin porous sensor films [8]. However, deposition of thick porous films ($>20\ \mu\text{m}$), as required by SOFC electrodes, remains a challenge because of the inherent low mechanical strength of the porous films.

A spray pyrolysis technique using an ultrasonic atomizer as an aerosol generator, as well as an electrostatic field to constrain the aerosol stream, was recently used in our laboratory to deposit $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) films on $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) substrates [9]. Although the symmetrical cells with LSCF electrodes showed comparable interfacial resistance values to those obtained with conventional processing routes [9,10], the thickness of the deposited films was much less ($\sim 4\ \mu\text{m}$) than that obtained by conventional routes ($\sim 30\ \mu\text{m}$) [10,11]. Because a thicker porous film was expected to offer more active reaction sites and hence better electrochemical performance, this work attempts to create such films. $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC), a promising SOFC cathode material

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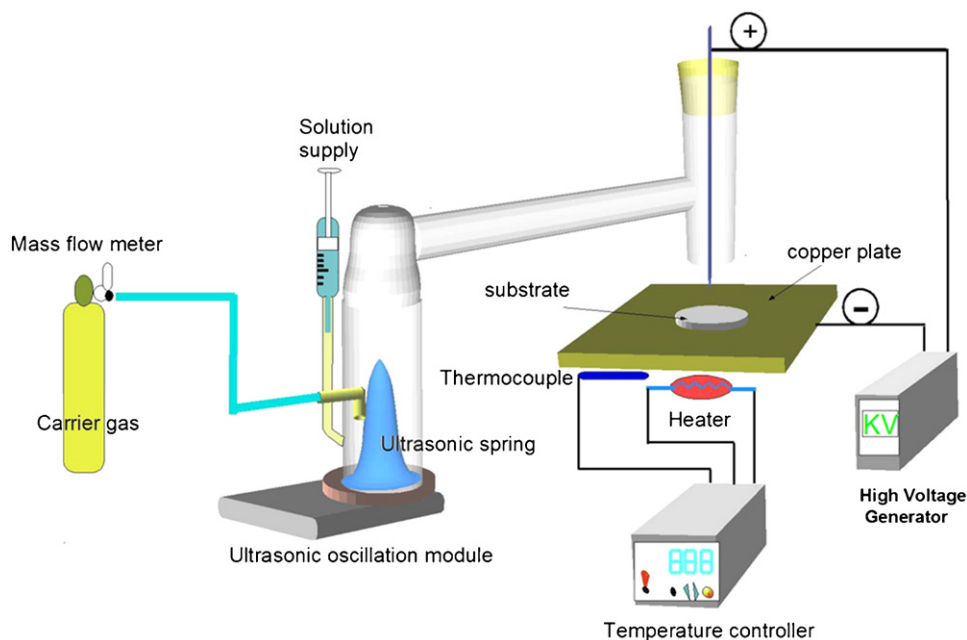


Fig. 1. A schematic diagram of the electrostatic assisted spray pyrolysis system.

[12], was selected and it was found that thick films ($>40\ \mu\text{m}$) with a unique porous columnar structure and low interfacial resistance values could be obtained by selecting the proper deposition temperature and electric field strength.

2. Experimental

In the spray pyrolysis deposition setup (Fig. 1), an ultrasonic atomizer was used to generate aerosol from a solution containing metal precursors. To constrain the aerosol stream and reduce the loss of expansive precursors to open air, an electrostatic field was employed to direct the aerosol droplets towards the substrate as the aerosol-carrying gas exited the guiding tube. The electrostatic field was established between the copper heating plate and the tip of a metal needle positioned at the exit of the guiding tube. A heater beneath the substrate was then used to promote pyrolysis of the aerosol droplets and formation of the desired oxide films.

In this work, the ultrasonic aerosol generator was operated at 1.65 MHz. The flow rate of carrying gas (N_2) was $1\ \text{l min}^{-1}$. The distance between the needle tip and the heating plate was 3 cm, while CGO disks of 15 mm diameter and 0.5 mm thickness were used as substrates. To prepare the starting solution for spray pyrolysis, nitrate precursors of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Strem chemicals, 99.9%), $\text{Sr}(\text{NO}_3)_2$ (Showa, 98%), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Showa, 98%) were dissolved into de-ionized water. The total concentration of metal ions in the starting solution was 0.4 M. A post-deposition calcination of $800\ ^\circ\text{C}/2\ \text{h}$ was carried out for each film to promote crystallization.

Phase identification was carried out for the calcined films using an X-ray powder diffractometer (Siemens D5000) with a Cu tube and a quartz monochromator on the diffracted beam side. A scanning electron microscope (SEM, Joel, JSM-6330) was used for observation of the surface and cross-section morpholo-

gies. Impedances of SSC//CGO//SSC symmetrical cells were measured using a potentiostat/galvanostat (Autolab PGSTAT30) with an excitation voltage amplitude of 50 mV. Pt paste was painted on the electrode surface to serve as charge collector. The ac impedance spectra were recorded over the frequency range of 0.003–100 kHz in the temperature range of 500–700 $^\circ\text{C}$ in ambient air.

3. Results and discussion

Thick porous films of a unique columnar structure were obtained with a deposition temperature of 400 $^\circ\text{C}$ and an applied voltage of 10 kV. Growth of columns with increasing deposition time is clearly seen in Fig. 2(a)–(f). The film thickness, as plotted in Fig. 3(a), increased from ~ 1 to 40 μm as the deposition time increased from 30 to 600 s. The identity of the crystalline perovskite phase was confirmed by X-ray diffraction as shown in Fig. 3(b). SEM close-ups in Fig. 4(a)–(c) indicate that oxygen/air can penetrate easily into the film interior not only through space between columns, but also through pores inside each column as the latter are large enough ($\sim 100\ \text{nm}$) to allow a quick diffusion of gas molecules. In addition, a layered structure inside each column is also clearly seen.

Typical impedance spectra of symmetrical cells with SSC electrodes are shown in Fig. 5(a). Area specific resistance (ASR) values, as determined from the intercepts of the arcs on the Z' axis, are plotted in Fig. 5(b). ASR values decreased with increasing electrode thickness as expected and reached constant values beyond a thickness of about 10 μm . This level off can be understood by considering the steps of the reduction reaction. Surface exchange reaction ($(1/2)\text{O}_2 + \text{V}_\text{O}^{\bullet\bullet} + 2\text{e}^- = \text{O}_\text{O}^{\times}$) and diffusion of oxygen ions in the mixed conductor are two potential rate determining steps in the cathode reduction process. Their rates are characterized by the surface exchange coefficient k (cm s^{-1})

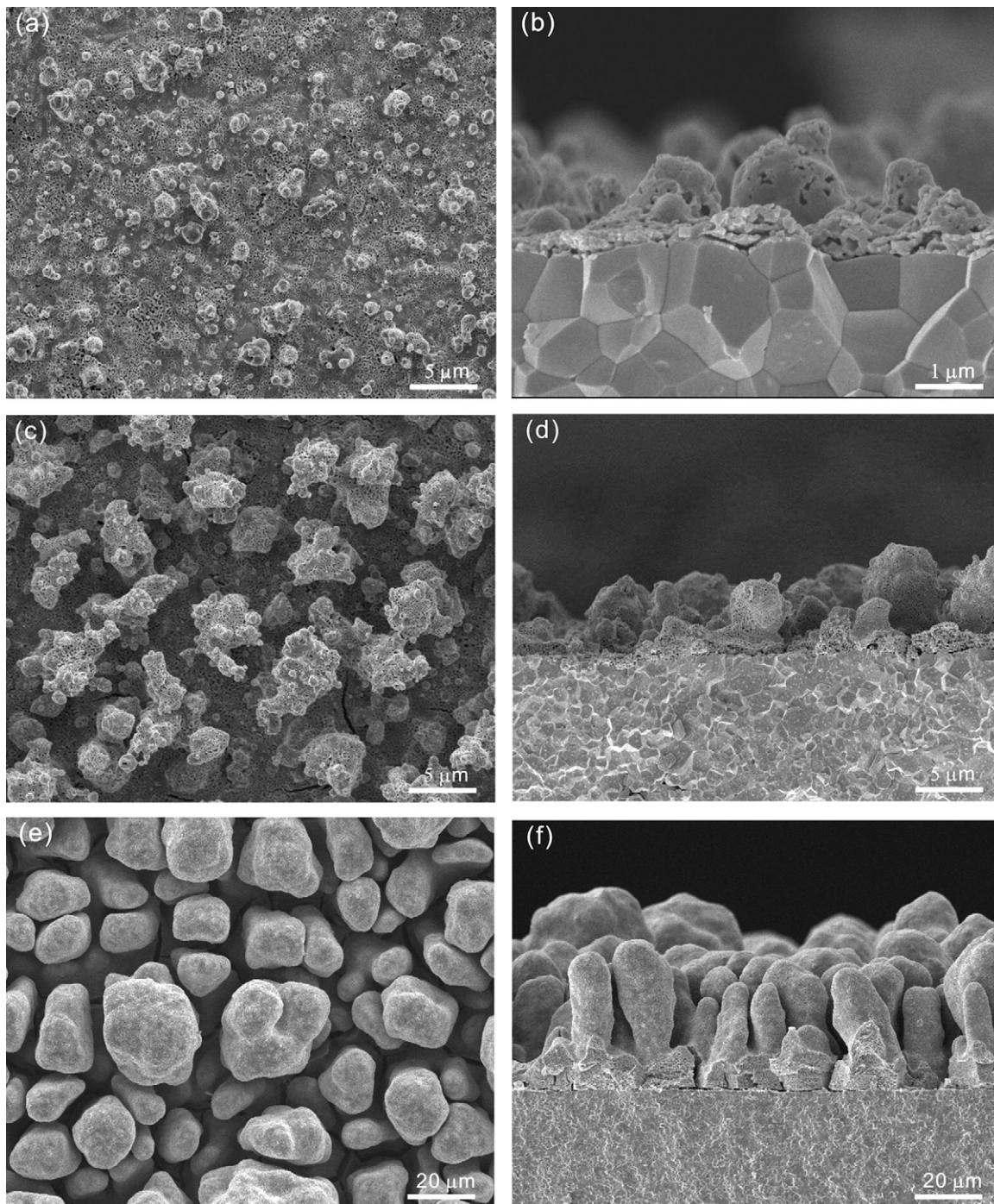


Fig. 2. SEM micrographs showing morphology of SSC films obtained with different deposition times: (a) 30 s, surface, (b) 30 s, cross-section, (c) 180 s, surface (d) 180 s, cross-section, (e) 600 s, surface, (f) 600 s, cross-section.

and the oxygen self-diffusion coefficient D^* ($\text{cm}^2 \text{s}^{-1}$) [13,14]. Although increasing the thickness of a porous electrode can raise the apparent surface exchange rate by providing more active reaction sites, the overall cathode reaction rate cannot be raised by increasing the thickness without bound because the length of the diffusion route for oxygen ions increases correspondingly. It has been shown that a characteristic length, L_c , which indicates the change-over from surface to bulk control, is given by D^*/k [15,16]. A collection of existing k and D^* data [13] for oxides

commonly used as SOFC cathode suggests that most L_c values are clustered around $100 \mu\text{m}$. Taking into account of the tortuosity, this is in accord with current results and the available data indicating that useful electrode thicknesses are limited to about $20\text{--}30 \mu\text{m}$ [13].

The ASR values obtained in this work were rather low, with minimum values of $0.20 \Omega \text{cm}^2$ at 600°C and $0.035 \Omega \text{cm}^2$ at 700°C . The corresponding values obtained with conventional process routes were much higher; for example, ASR values at

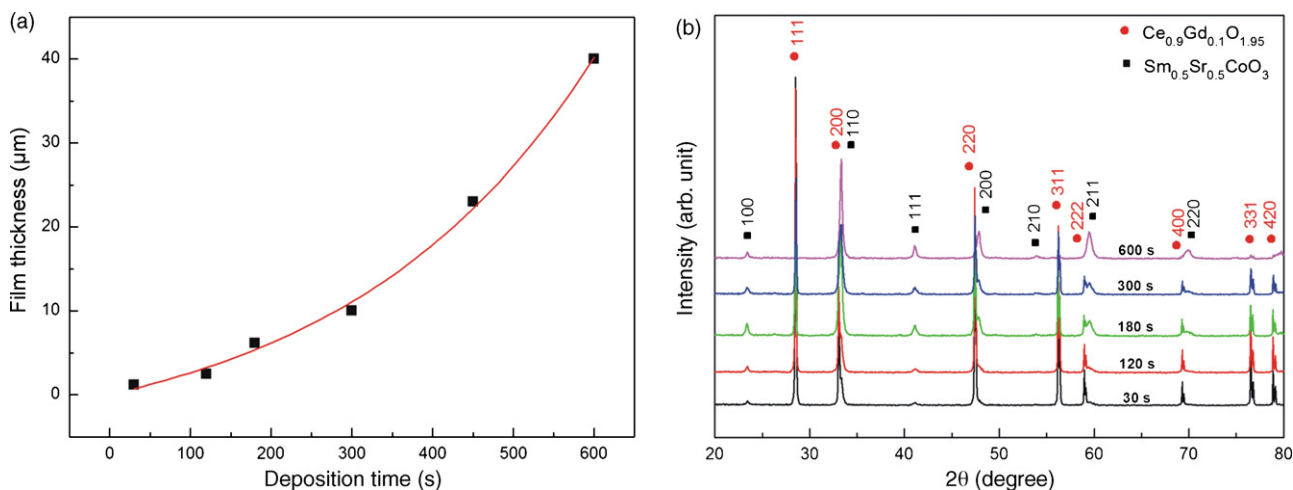


Fig. 3. (a) Film thickness as a function of deposition time and (b) XRD patterns of SSC films on CGO substrates.

600°C obtained by Xia et al. by slurry painting [17] and Lv et al. by screen-printing [18] were 1.73 and $2.40 \Omega \text{cm}^2$, respectively.

4. Conclusion

Thick ($>40 \mu\text{m}$) porous SSC films of a unique columnar structure were obtained using ultrasonic spray pyrolysis assisted by an electrostatic field under a deposition temperature of 400°C

and an applied voltage of 10 kV . The high porosity and high thickness of these films resulted in very low ASR values of SSC//CGO//SSC symmetrical cells: the minimum values were 0.20 and $0.035 \Omega \text{cm}^2$ at 600 and 700°C , respectively.

The excellent mechanical strength, good adhesion to substrates, high thickness and high porosity of films obtained in this work make them ideal for SOFC operation. Also, the high deposition rate, ease of operation in open air and low cost make

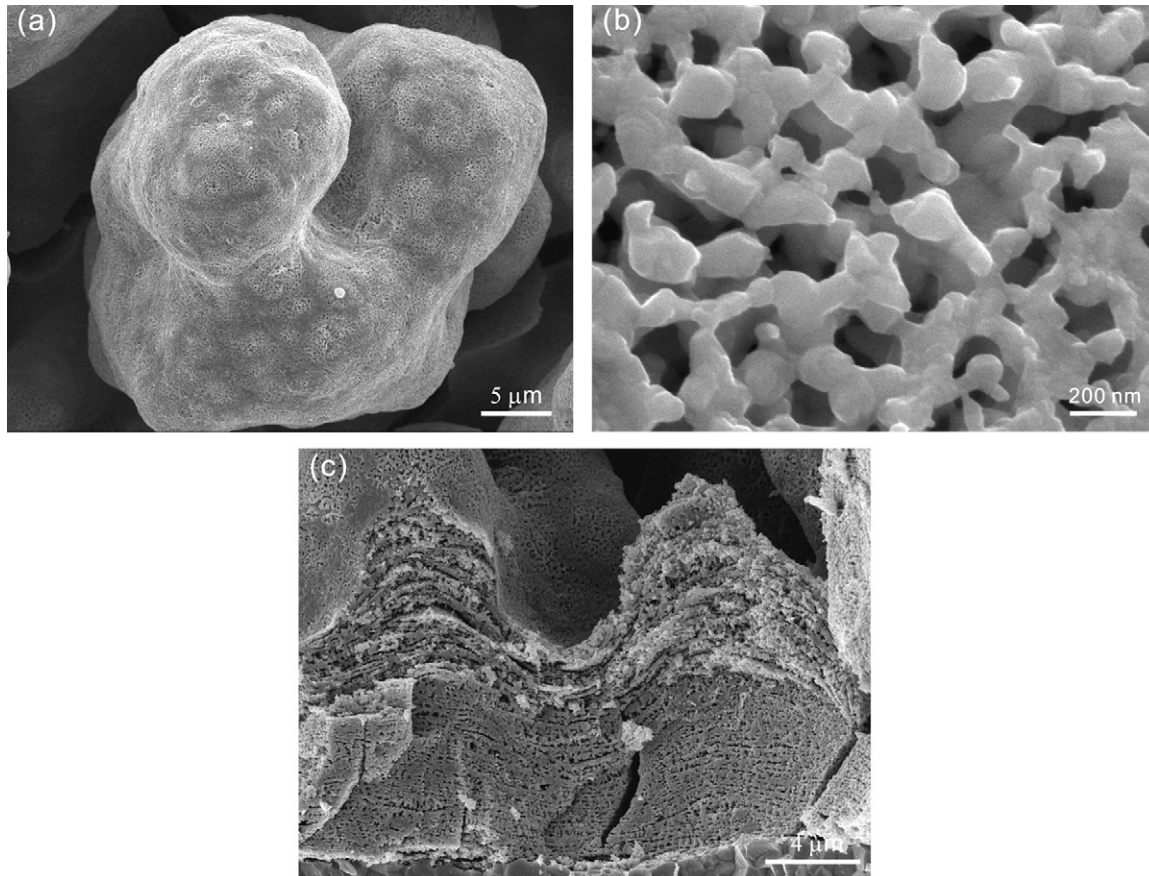


Fig. 4. SEM close-ups of films obtained at a deposition time of 600 s , showing: (a) top view of a single column, (b) pores in (a), and (c) cross-section.

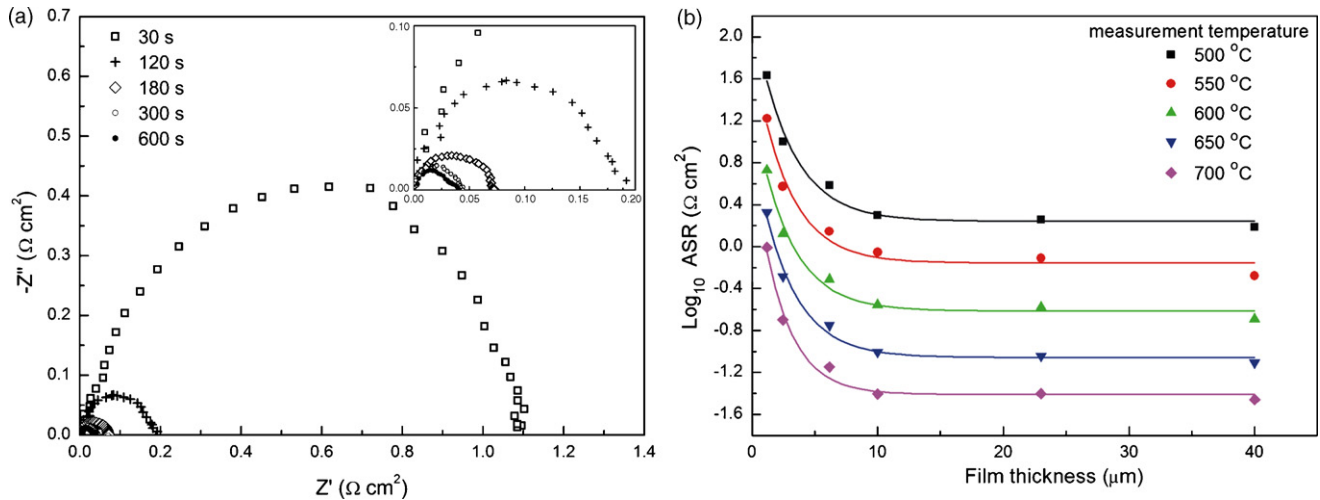


Fig. 5. (a) ac impedance spectra of SSC//CGO//SSC cells measured in ambient air and 700 °C (b) interfacial ASR values as determined from impedance spectra at different measurement temperatures.

the ultrasonic spray pyrolysis assisted by an electrostatic field a particularly useful method for preparation of such films.

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