

Thermoelectric hydrogen sensor using $\text{Li}_x\text{Ni}_{1-x}\text{O}$ synthesized by molten salt method

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Abstract—Li-doped NiO was synthesized by molten salt method. LiNO_3 -LiOH flux was used as a source for Li doping. NiCl_2 was added to the molten Li flux and then processed to make the Li-doped NiO material. Li:Ni ratios were maintained from 5 : 1 to 30 : 1 during the synthetic procedure and the chemical compositions after characterization were found from $\text{Li}_{0.08}\text{Ni}_{0.92}\text{O}$ to $\text{Li}_{0.16}\text{Ni}_{0.84}\text{O}$. Li doping did not change the basic cubic structural characteristics of NiO as evidenced by XRD studies; however, the lattice parameter decreased from 0.41769 nm in pure NiO to 0.41271 nm in $\text{Li}_{0.16}\text{Ni}_{0.84}\text{O}$. Hydrogen gas sensors were fabricated by using these materials as thick films on alumina substrates. The half surface of each sensor was coated with the Pt catalyst. The sensor, when exposed to the hydrogen gas blended in air, heated up the catalytic surface leaving the rest half surface (without catalyst) cold. The thermoelectric voltage thus built up along the hot and cold surface of the Li-doped NiO made the basis for detecting hydrogen gas. The linearity of the voltage signal vs H_2 concentration was checked up to 4% of H_2 in air (as higher concentrations above 4.65% are explosive in air) using $\text{Li}_{0.10}\text{Ni}_{0.90}\text{O}$ as the sensor material. The response time T_{90} and the recovery time RT_{90} were less than 25 sec. H_2 concentration from 0.5% to 4% showed a good linearity against voltage. There was minimum interference of other gases and hence H_2 gas can easily be detected.

Key words: Li-Doping, NiO, Molten Salt Method, Thermoelectric Gas Sensor, Hydrogen

INTRODUCTION

NTC (negative temperature co-efficient) thermistors find their applications in electronics especially for temperature control and measurements [Vakiv et al., 2004]. Most of the materials used in practice are the solid solutions of transition metal oxides viz. NiO, Co_3O_4 , Fe_2O_3 , Mn_3O_4 etc. [Vakiv et al., 2004; Schmidt and Brinkman, 2001]. NiO is an attractive material used as p-type transparent conducting films [Sato et al., 1993] and sensing materials in chemical sensors [Hotovy et al., 2000, 2001, 2002; Dirksen et al., 2001]. It is a good thermoelectric oxide material and its conductivity is controlled easily by doping with mono-valent impurities like Li^+ or Na^+ [Wu et al., 2002] and substitution of Li for Ni atoms in NiO results in a high thermoelectric power factor over a wide temperature range [Shin et al., 2001].

Recently, the Murayama group in Japan at National Institute of Advanced Industrial Science and Technology (AIST) has exploited the thermoelectric materials as hydrogen gas sensors [Qiu et al., 2003, 2004; Matsumiya et al., 2002, 2003; Shin et al., 2003, 2004], where they utilized Pt catalyst with a thermoelectric material in most of the cases. The principle is simple. The thermoelectric material film with Pt catalyst on the half part of the fabricated film heats up on Pt coated surface when exposed to hydrogen and rest of the half film with thermoelectric (without Pt) film remains cold, thereby building up of a thermoelectric voltage. This property plays an important role for the detection of hydrogen gas. Very few papers have appeared on the use of Li-doped NiO as thermoelectric material for hydrogen gas detection, that too by Murayama group [Matsumiya et al., 2002, 2003; Shin et al., 2003, 2004]. In these publications

they did not describe dependence between Li-doping amount and hydrogen sensing ability.

In this study, we prepared various amounts of Li-doped NiO material by a molten salt method. A LiNO_3 -LiOH mixture was taken as the flux material and Ni salt was added in the molten flux. Different compositions of the Li-doped materials obtained were characterized and were screen-printed as thick films for their possible use as thermoelectric materials for the hydrogen gas sensor.

EXPERIMENTAL

1. Synthesis and Characterization of the Li-doped NiO Material

A flux composition with 0.59 LiNO_3 -0.41 LiOH, eutectic melting point 183 °C [Hong et al., 2000], was used as a lithium source. Appropriate amounts of LiNO_3 and LiOH were mixed in a pestle and mortar and brought to the molten state in an alumina crucible by heating at 480 °C for 24 h in air. The heating rate was set at 200 °C/h at all stages. Varying amounts of solid NiCl_2 (in a 1/5 to 1/30 mole ratio with respect to Li flux) were poured into the flux melt. After heating at 500 °C for 12 h the powders obtained were cooled and washed thoroughly with de-ionized water to remove all the residual flux material. Finally the products were oven-dried at 120 °C for 24 h. The crystal structures of the Li-doped NiO were obtained by X-ray diffraction with a Rigaku X-ray Diffractometer, D/Max 2000-Ultima with $\text{CuK}\alpha$ radiation. The morphologies and microstructures were examined by using a field emission scanning electron microscope (FE-SEM, Hitachi S-4300). The chemical compositions were determined by using an inductively coupled plasma spectroscope (ICP, Perkin Elmer ICP-52S).

2. Fabrication of the Sensor

The sensor was fabricated as shown in Fig. 1 by a screen-printing

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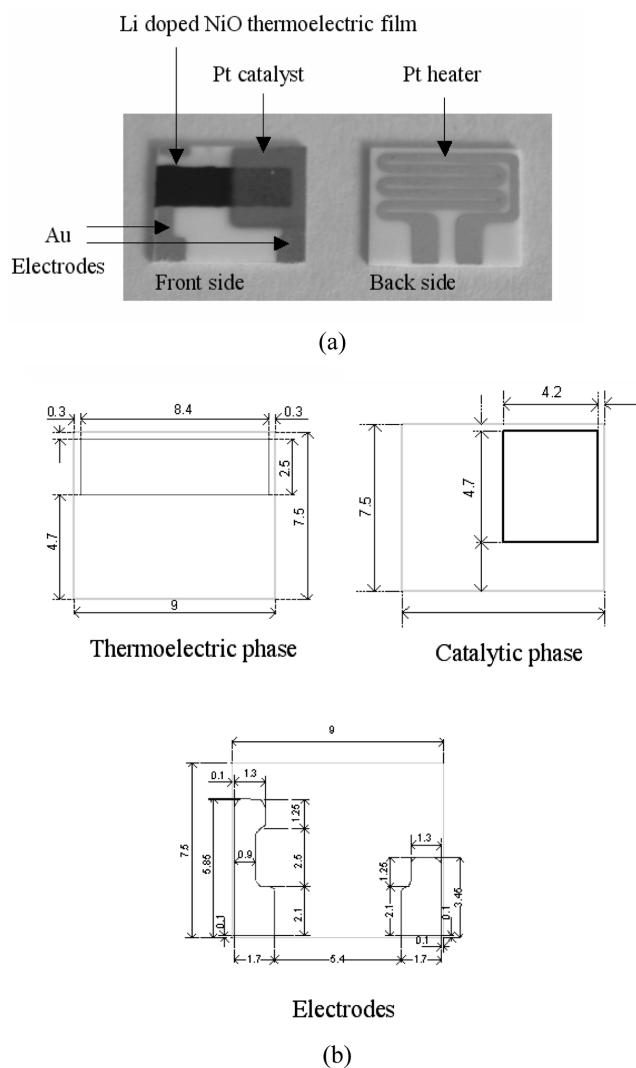


Fig. 1. Schematic diagram of the fabricated sensor (a) and its detailed drawings (b). Dimensions are in mm.

method. Appropriate amount of Li-doped NiO was mixed with ethylcellulose and terpinol and then screen printed on the alumina substrate. The layer was dried at 120 °C for 15 min, and then calcined at 800 °C for 2 h. A thin film of Pt was deposited at room temperature by an ion coater on half of the NiO surface with a metal mask. The details of the size of the device, Li-doped NiO layer and the Pt catalyst covered half of the oxide layer, are presented in the Fig. 1. Hydrogen gas sensing properties were evaluated in a gas chamber (size: 15×10×10 cm³). Hydrogen gas was mixed with pure air by using a manual gas blender and led to the measuring chamber. The operating temperature was set at 100 °C throughout the experiments while sensing the hydrogen gas. The electric voltage of the sensor element in air (V_o) and in a gas mixture (V_g) was measured.

RESULTS AND DISCUSSION

1. Characterization of the Materials

One of the advantages of the present molten salt method is that the eutectic mixture 0.59 LiNO₃-0.41 LiOH taken as flux had a eutectic melting point at 183 °C [Hong et al., 2000] and therefore the

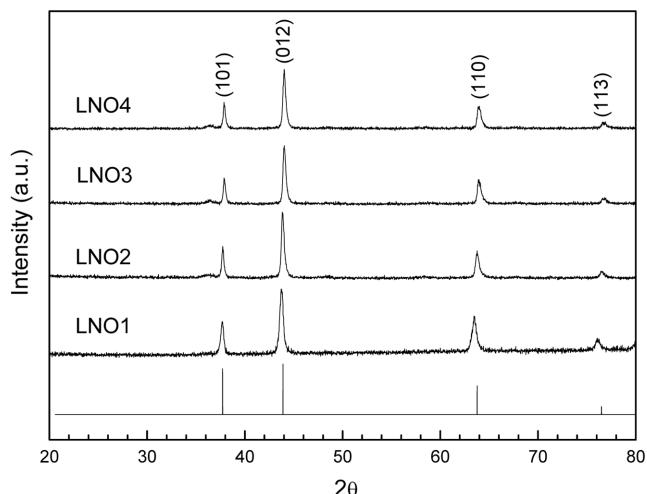


Fig. 2. XRD patterns of the synthesized Li-doped NiO with compositions as in Table 1.

Table 1. Synthetic conditions, chemical compositions, cell parameters of the samples

Sample	Synthetic condition	Chemical composition	Cell parameter (a)*
LNO1	Li ion/Ni ion=5	Li _{0.08} Ni _{0.92} O	4.158(8)
LNO2	Li ion/Ni ion=10	Li _{0.10} Ni _{0.90} O	4.144(7)
LNO3	Li ion/Ni ion=20	Li _{0.13} Ni _{0.87} O	4.131(9)
LNO4	Li ion/Ni ion=30	Li _{0.16} Ni _{0.84} O	4.127(1)

*Cell parameter was calculated by Valpas program.

doping of lithium could be done at much lower temperatures. The powder XRD results showed that the sample was in a single phase of Li-NiO solid solution. The XRD patterns, as shown in Fig. 2, showed minor change in the lattice constants of the cubic phase of NiO (Table 1). No evidence of any phase separation was noticed. The chemical compositions in each case were determined by inductively coupled plasma spectroscopy and the possible compositions obtained with their synthetic conditions are presented in Table 1. The microstructures, as shown in Fig. 3, determined by field emission scanning electron microscopy confirmed the size of the particles in a narrow range of ~200 nm.

The electric conductivities were measured in the temperature range from 20 to 160 °C. In samples LNO1 to LNO4 (Table 1), as the concentration of lithium increased from 0.08 to 0.16 mole the conductivity also increased at all measured temperatures as shown in Fig. 4. This showed the increase in conductivity is a function of temperature and increased with the rise of temperature. Most probably a single phase is formed if lithium concentration is 1/8 of the nickel concentration with a composition of LiNi₇O₈ [Mackrodt et al., 1996]. In both the cases i.e. LNO2 and LNO3, the lithium concentration is around 1/8 of Ni atoms and hence conductivity is almost same in these cases.

2. Effect of Li-doping

XRD studies of the Li-doped NiO indicated a similar cubic crystal structure with somewhat smaller unit cell than pure NiO. Pure NiO showed a bunsenite (syn) structure with a cubic lattice param-

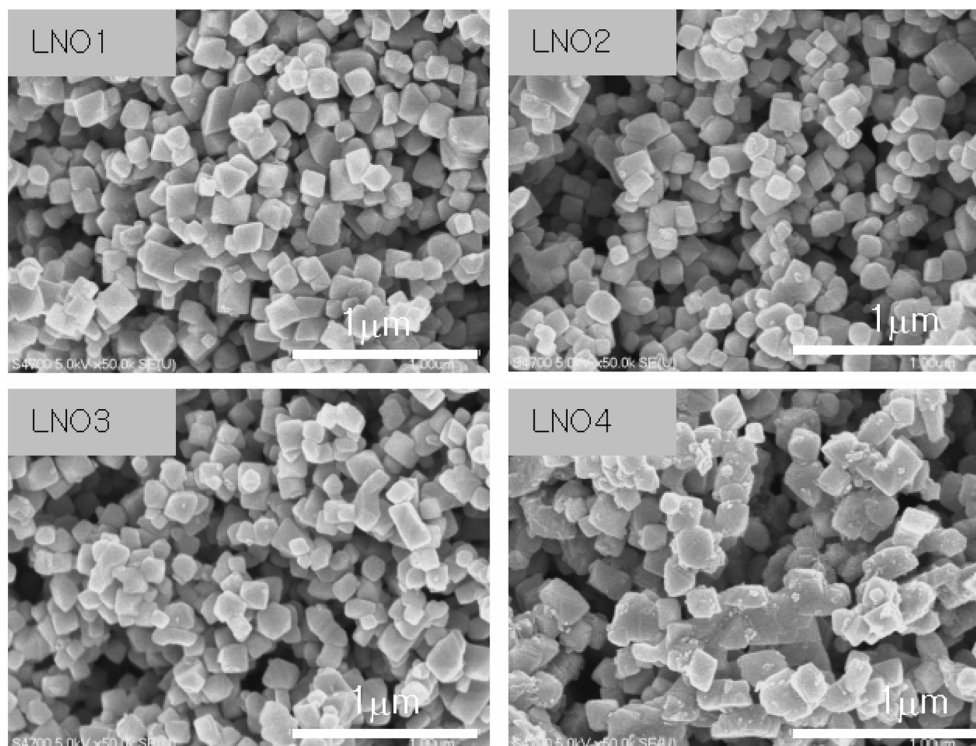


Fig. 3. FE-SEM photographs of synthesized Li-doped NiO.

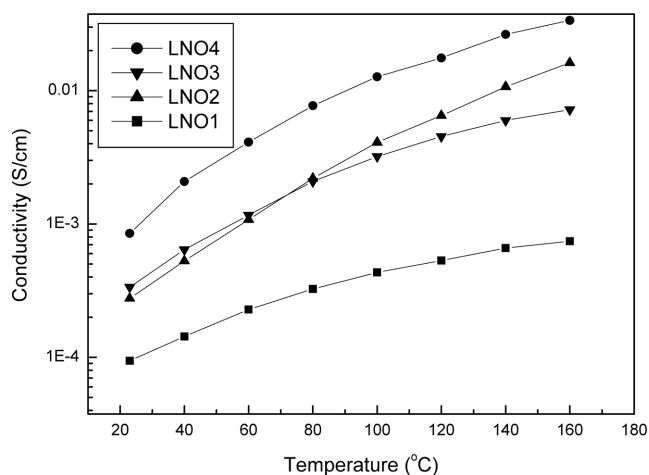


Fig. 4. Relation between the conductivities of the Li-doped NiO against temperature.

eter of 0.41769 nm according to the JCPDS Card No. 04-0835 [1994]. Our studies, as shown in Table 1, confirmed that the cubic structure was maintained with the lithium doping. The lattice parameters slightly decreased with increasing lithium concentration doping in NiO, maximum fall being in $\text{Li}_{0.16}\text{Ni}_{0.84}\text{O}$ having a lattice parameter of 0.41271 nm. The Fm3m space group was maintained in all the cases as in pure NiO.

NiO is slightly off-stoichiometric due to its p-type semi-conducting characteristics, resulting in a deficiency in metal ions compared to oxygen ions, affecting thereby the electrical conductivity. Metal deficiency in p-type oxide leaves a metal vacancy in the crystal, which

is charge compensated by an electron in its electronic structure. Thus oxygen partial pressure in the atmosphere plays an important role in its electrical conductivity. Alkali metal ions like Li^+ or Na^+ are easily doped in the NiO lattice, to create more crystal imperfection. These cations sit on the cation lattice site but with a lower valency. Since the charge on lithium is +1, less than compared to nickel, less charge on this impurity is compensated by more metal vacancies in the crystal structure, thus increasing more holes at energies within the band gap. The addition of Li ions to NiO therefore results in the formation of cations of increased valency, i.e., Ni^{3+} . This effect increases the intrinsic conductivity of NiO from $10^{-8} (\Omega \cdot \text{cm})^{-1}$ at 500 K to $1 (\Omega \cdot \text{cm})^{-1}$ with the addition of 10 at% of Li [Zainullina et al., 2004; Mackrodt et al., 1996].

3. Hydrogen Gas Sensing Properties

Observations showed that Li-doping NiO sensor gave higher conductivity than the undoped NiO sensor, allowing much lower applied voltage with a good baseline stability. O_2 partial pressure plays an important role in the electrical conductivity of this material [Dirksen et al., 2001], and hence the presence of a reducing gas, especially H_2 [Shin et al., 2003, 2004; Matsumiya et al., 2002], at the surface decreases the partial pressure of O_2 altering the electrical conductivity. In the present studies 3% of the H_2 gas in air was taken as the target gas as higher concentrations (above 4.65%) lead to explosion and therefore the linearity tests were made up to 4% H_2 gas in air. The gas response was performed in a gas chamber with switching to pure air and hydrogen samples alternatively.

Fig. 5 shows the response times of the fabricated sensors by using different synthesized materials given in Table 1 against 3% H_2 gas. Maximum change in voltage was seen in case of material LNO2. This change may be due to the increase of intrinsic conductivity with

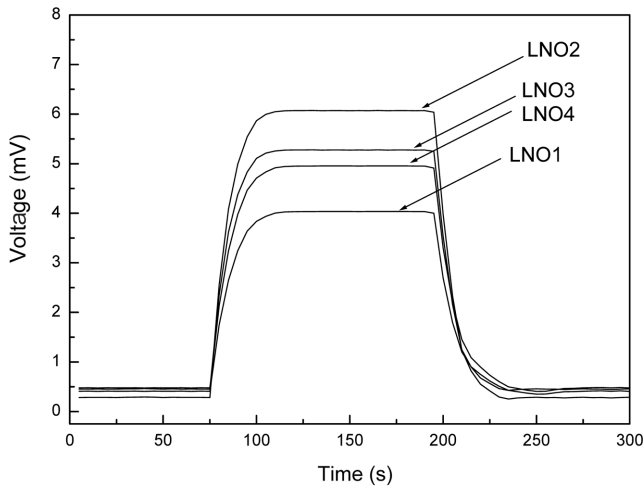


Fig. 5. Response profiles of the fabricated sensors against 3% H_2 gas.

the addition of 10 at% of lithium [Zainullina et al., 2004; Mackrodt et al., 1996]. Zainullina et al. [2004] showed in their calculations on the cohesive energy of $Li_xNi_{1-x}O$ crystals that $Li_{0.125}Ni_{0.875}O$ phase is the most stable and probably the phase formed is $LiNi_7O_8$ [Mackrodt et al., 1996]. In our study, SEM photographs also showed that the crystalline phase is not well defined with lithium concentration at 16 at%, which may be due to the mixed crystalline phases of $LiNi_7O_8$ and $LiNi_3O_4$ [Mackrodt et al., 1996] and the first phase may have the higher sensitivity for hydrogen gas.

Doping amount higher than 10% of Li in NiO decreased the sensitivity against H_2 gas. As can be seen from the Fig. 5, the response time T_{90} , the time at which 90% saturation level in voltage was reached, was less than 25 sec in all the materials used. Similarly, the recovery time RT_{90} , the time to return back to 90% of the original voltage level, was about 18 sec. The baseline for the voltage was very stable without any fluctuation and no drift was observed if different concentrations of H_2 were used within the permissible limits. The results showed that the highest sensitivity was observed when LNO2 material was used, and hence in subsequent studies this ma-

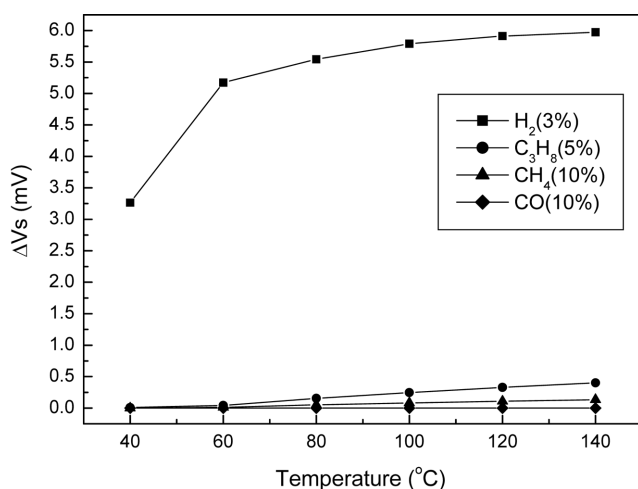


Fig. 6. Sensing behavior of the LNO2 sensor against different gases vs. temperature.

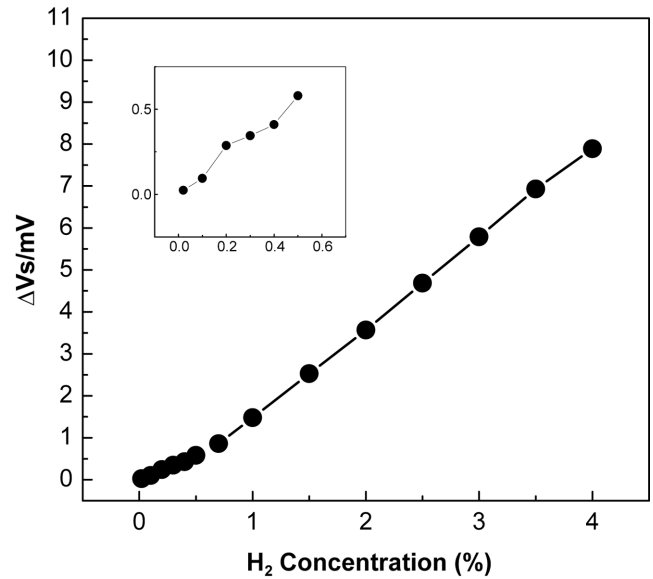


Fig. 7. Change in voltage signal of the LNO2 sensor against H_2 gas concentration.

terial was chosen as the sensor material.

The effect of temperature on sensing the fixed concentration of H_2 gas at 3% level with the sensor material LNO2 showed (Fig. 6) that the change in voltage was lowest at 40 °C, but abruptly increased up to 60 °C thereafter, slowly increasing with increasing temperatures. Sensing characteristics increased with increasing ambient temperature because of the higher interaction of hydrogen molecules with the material. However little changes were observed from 80 to 120 °C; hence, in our studies the temperature was maintained at 100 °C. Other gases like CO (5%), CH_4 (10%) and C_3H_8 (10%) showed almost negligible response in comparison to H_2 gas, as shown in Fig. 6. It means the H_2 gas can easily be detected in the presence of these gases.

Fig. 7 shows the measured voltage signals exposed to varying H_2 concentration diluted in air. The hydrogen gas was varied from 0.2% to 4% at normal atmospheric pressure with balance of air. The results below 0.2% of H_2 were not accurate and the signals had fluctuations. However, with the H_2 concentrations from 0.5% to 4% showed a good linearity and the voltage signals were stable. Concentrations higher than 4% of H_2 gas in air were not investigated.

Ambient condition dependence of the thermoelectric sensor was also tested in the temperature and humidity test chamber. The temperature dependence test was investigated in the range from 0 °C to 60 °C by increasing 10 °C temperature at each step, keeping relative humidity percent (%Rh) maintained at 50%. Similarly, a humidity dependence test was carried out from 10% to 70% increasing 10% relative humidity, maintaining the temperature at 20 °C. Almost no effect was observed in this condition range. Voltage change in this test range was less than 0.3 mV.

CONCLUSION

Li-doped NiO materials prepared by molten salt method gave single phase of Li-NiO solid solutions having particle size ~200 nm. Doping of Li into NiO increased the conductivity of the NiO sem-

iconductor; hence, a lower voltage could be used for detection of H₂ gas. The hydrogen gas sensors were fabricated with the synthesized materials. The best material selected gave a response time T₉₀ less than 25 sec and a recovery time RT₉₀ of about 18 sec. The baseline for the voltage was very stable without any fluctuation. H₂ concentration from 0.5% to 4% showed good linearity against voltage. There was minimum interference of other gases like CO, CH₄, C₃H₈ etc., and hence the presence of H₂ gas can easily be detected. Sensor test showed that this thermoelectric sensor was little affected by ambient temperature and humidity.

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