SYNTHESIS AND CHARACTERIZATION OF $La_2Mo_2O_9$ SOLID OXIDE-ION CONDUCTOR PREPARED BY AN AQUEOUS SOL-GEL METHOD

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INTRODUCTION

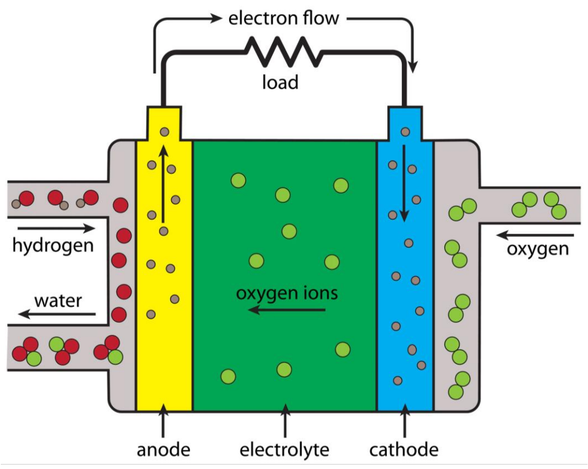
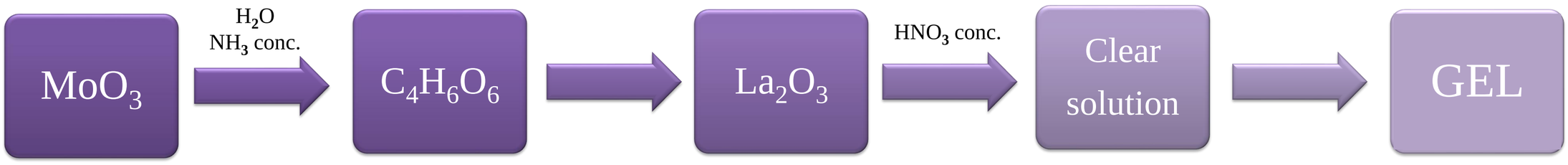


Fig. 1 Solid oxide fuel cell.

Fuel cells were discovered by William Grove in early 1839. The basic operating principle of these devices is to generate electricity and heat from hydrogen and oxygen as long as fuel and oxidant are supplied. Comparing these devices with other conventional and distributed generation systems it was observed that the energy efficiency of fuel cells is always higher and pollution emissions are much lower. Solid-oxide fuel cells (SOFCs) are one of the most environmentally friendly and efficient technologies to produce electric power and heat. Nowadays, the most widely used materials for a SOFC electrolyte are yttria-stabilized zirconia (YSZ) and gadolinium-doped ceria (GDC). However, these materials require a high-operating temperature (1000 °C) to obtain high oxide-ion conductivity. In 2000, Lacorre et al. discovered a new family of oxide ion conductors with parent compound $La_2Mo_2O_9$. Lanthanum molybdate undergoes a reversible transition from monoclinic α-phase to cubic β-phase structure at 580 °C, leading to an increase in the ionic conductivity up to two orders of magnitude and reaching values higher than those corresponding to YSZ.

Currently, there are various ways to synthesize LAMOX compounds, and it is known that the thermal decomposition mechanism and phase transition strongly depends on the preparation method. Lanthanum molybdate ceramic synthesized by such methods as solid-state route, citrate, a Pechini, the microwave-assisted, and EDTA complexation methods usually contain impurities, and the obtained compound has a porous structure. To eliminate these drawbacks, a lot of attention has been drawn to wet-chemical methods. The simplest, cheapest and most environmentally friendly method is an aqueous sol-gel synthesis, which creates an opportunity to control the final ceramic structure, crystallites size and morphology.

AQUEOUS SOL-GEL SYNTHESIS SCHEME



TGA-DTG-DSC ANALYSIS

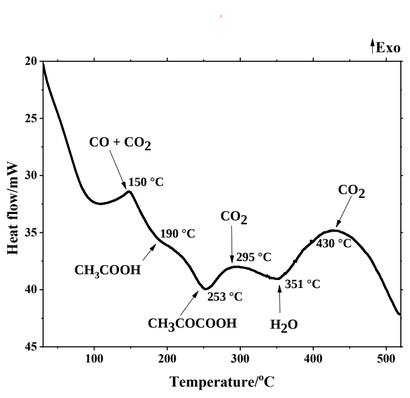


Fig. 2 DSC curve of the $La_2Mo_2O_9$ tartrate precursor gel in flowing air.

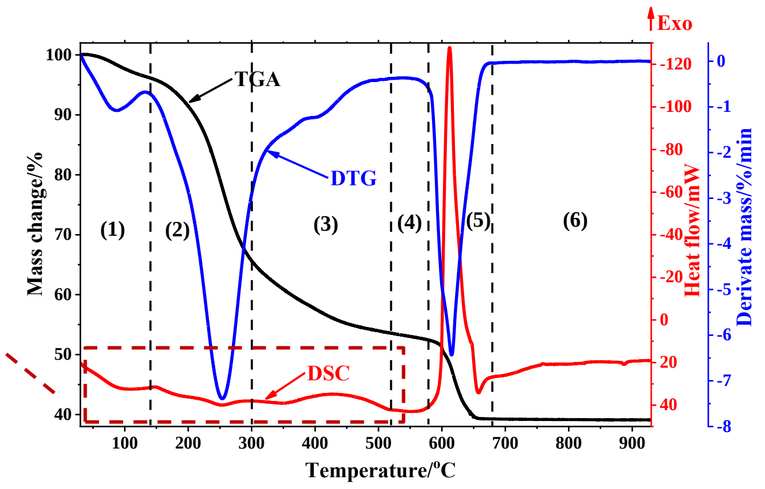


Fig. 3 TGA-DTG-DSC curves of the $La_2Mo_2O_9$ tartrate precursor gel in flowing air.

$$MoO_3\ (s) + 2\ NH_3 \cdot 2\ H_2O\ (aq) \rightarrow (NH_4)_2MoO_4 \cdot H_2O\ (aq)$$

$$p\ (NH_4)_2MoO_4\ (aq) + q\ C_4H_6O_6\ (aq) \rightarrow [(MoO_4)_p(C_4H_4O_6)_qH_r]^{(2p+2q-r)-}\ (aq) + 2p\ NH_4^+\ (aq)$$

$$La_2O_3\ (s) + 6\ HNO_3\ (aq) \rightarrow 2\ La(NO_3)_3\ (aq) + 3\ H_2O\ (l)$$

$$[(MoO_4)_p(C_4H_4O_6)_qH_r]^{(2p+2q-r)-}\ (aq) + p\ La^{3+}\ (aq) \rightarrow La_p[(MoO_4)_p(C_4H_4O_6)_qH_r]^{3p-(2p+2q-r)}\ (aq)$$

$La_p[(MoO_4)_p(C_4H_4O_6)_qH_r]^{3p-(2p+2q-r)}$ (aq) + 3p $C_4H_4O_6$ (aq) + 3p NO_3^- (aq) —Dried at 120 °C→ GEL

- $La_p[(MoO_4)_p(C_4H_4O_6)_qH_r]^{3p-(2p+2q-r)}$ (aq): **Metal tartrates**
- 3p $C_4H_4O_6$ (aq): **An excess of tartaric acid**
- 3p NO_3^- (aq): **Residual nitrates**

XRD ANALYSIS

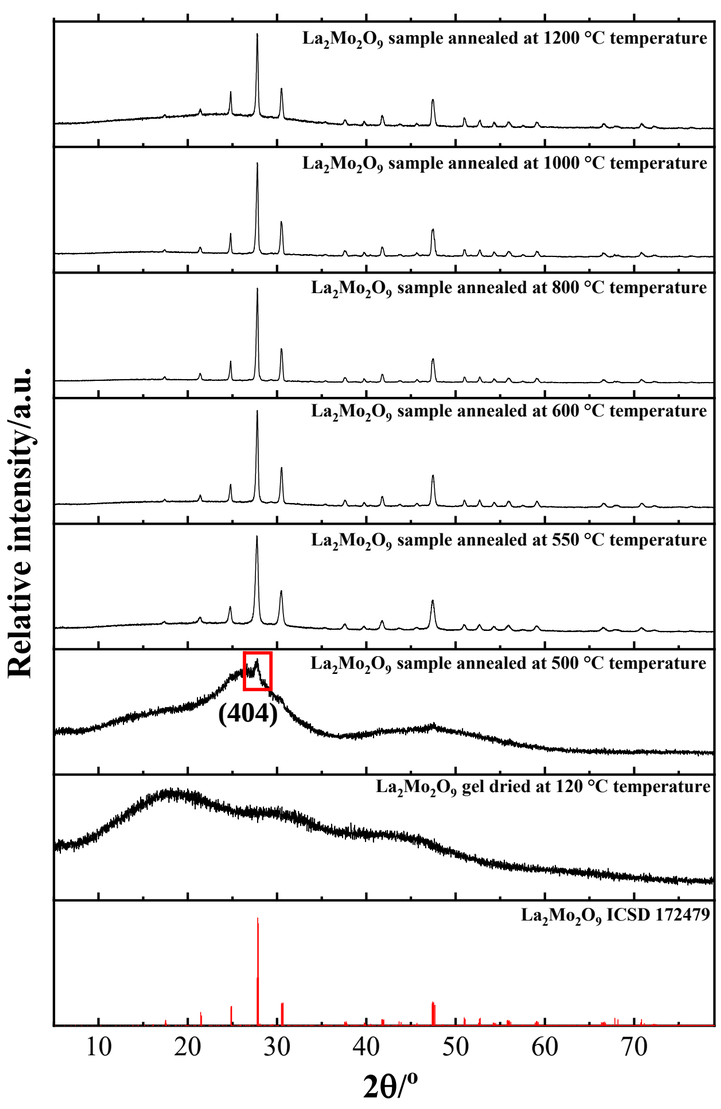


Fig. 4 XRD patterns of the $La_2Mo_2O_9$ tartrate gel precursors annealed at different temperatures.

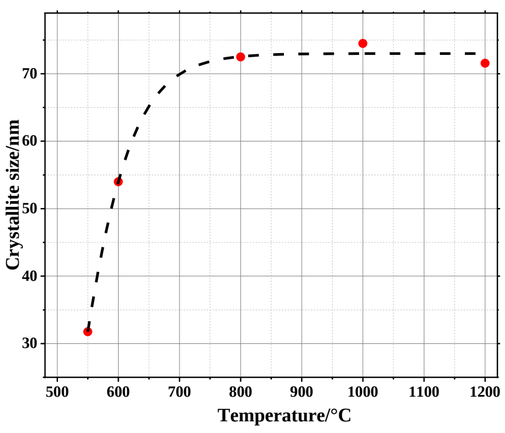


Fig. 5 Plot of crystallite size versus heat-treatment temperature for $La_2Mo_2O_9$ ceramic.

PHASE TRANSITION AND ELECTRICAL PROPERTIES

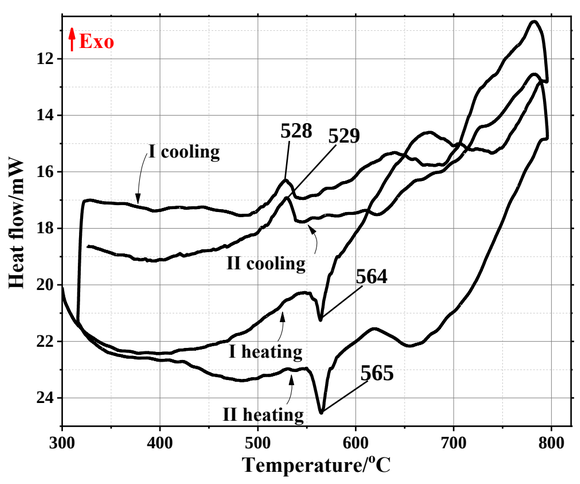


Fig. 6 DSC curve of the $La_2Mo_2O_9$ ceramic heat-treated at 1200 °C of temperature.

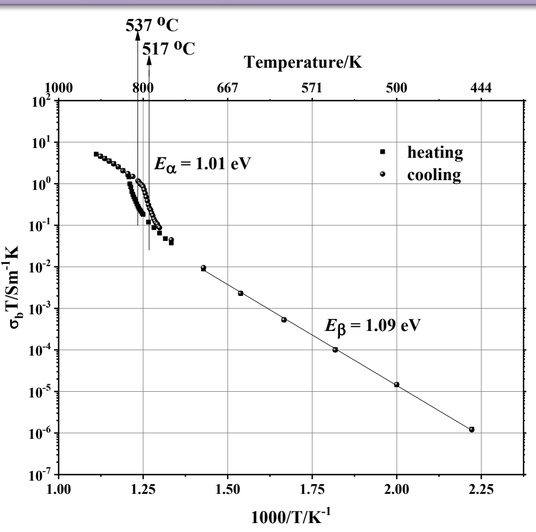


Fig. 7 Arrhenius plots of temperature dependencies of standard deviation for α- and β-phase transition processes in $La_2Mo_2O_9$ ceramic.

SEM ANALYSIS

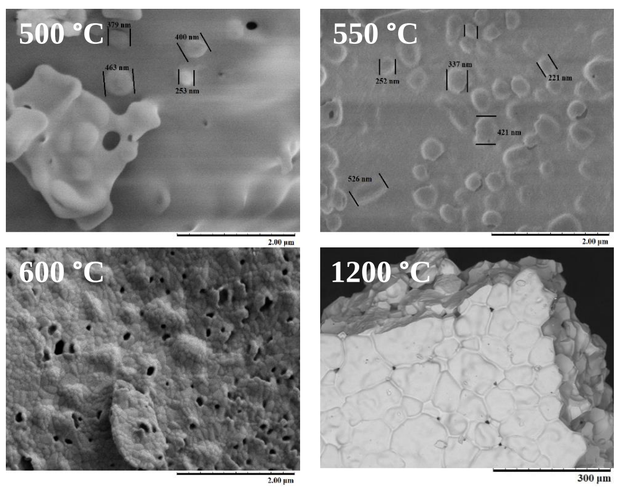


Fig. 8 SEM micrographs of $La_2Mo_2O_9$ ceramic heat-treated at different temperatures.

CONCLUSIONS

In conclusion it is clear that the $La_2Mo_2O_9$ oxide-ion conductors could be successfully prepared by an aqueous sol-gel synthesis method using tartaric acid as a complexing agent. The TGA-DTG-DSC analysis showed that thermal decomposition of La–Mo–O tartrate gel precursors could be divided into at least six parts. It was observed that crystalline phase of lanthanum molybdate forms at the temperature below 680 °C. DSC investigation revealed that phase transition from α-phase to β-phase occurs in the higher temperatures (from 555 °C to 570 °C) than the opposite process (from 514 °C to 538 °C). Besides, slightly lower activation energy of monoclinic phase (1.01 eV) formation than of cubic phase (1.09 eV) shows that low-temperature phase is more stable. X-ray diffraction results indicated that from 550 °C temperature pure monoclinic phase of lanthanum molybdate formed. The surface morphology of the samples is well developed with well-connected grains and very low porosity.