

Study on the Effect of Proportion of Citric Acid to the Structure of Perovskite LaNiO_3

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Abstract: Perovskite LaNiO_3 which is used in bifunctional oxygen electrode is prepared by the sol-gel method using citric acid as complexing agent. Products are characterized using TG-DTA, XRD, SEM, et al. It showed that the proportion of citric acid have major influences on cination of dried polymer, the structure and component of LaNiO_3 . Uniformly nanoscaled LaNiO_3 bar is got when the proportion of lanthanum nitrate, nickel nitrate and citric acid is between 1:1:0.6 and 1:1:0.7. Furthermore, the effect of sufficient or insufficient proportion of citric acid to the formation and cination of sol-gel to the purity of phases and spatial structures of LaNiO_3 are discussed.

Key words: LaNiO_3 ; sol-gel method; citric acid; perovskite oxides

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Bifunctional oxygen electrode has received extensive attention in recycle fuel cell and metal-air batteries because of its high catalytic activity and stability. Many kind of catalyst methods^[1-3]: noble metal, sole metal oxide, metal organic chelate, transition metal carbonyl compounds and metal complex compounds are used in bifunction oxygen electrode. Perovskite complex compounds became the most promising role due to its advantage which inexpensive cost, antioxygenic properties and high catalytic activity. Presently, $\text{La}_{0.6}\text{Ca}_{0.4}\text{O}_3$ has been in application in charged zinc oxygen battery^[3] and metal cyanide air battery^[4] for high electrocatalytic activity. In this paper, LaNiO_3 is prepared by the sol-gel method using citric acid as complex agent.

1 Experiment

The LaNiO_3 perovskite catalyst is prepared by sol-gel method as follows. 0.05 mol/L solution is produced by which stoichiometric ratio $\text{La}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_3$ is dissolved in twice distilled water, and then 0.02 mol/L $\text{C}_6\text{H}_8\text{O}_7$ is added in above mentioned solution, the proportion of $\text{La}(\text{NO}_3)_3$: $\text{Ni}(\text{NO}_3)_3$: $\text{C}_6\text{H}_8\text{O}_7$ changed from 1:1:0 to 1:1:5.0. 60~80 °C, LaNiO_3 catalyst is synthesized by calcination of the dried gel.

A Japan Rigaku D/max 2500 V/PC X-ray diffractometer (Cu, $\lambda=0.154178$ nm) is used for the XRD analysis of the catalyst. 2 θ : 20~80°.

A TACHIX-650 scanning electron microscope is used for overall microstructure and appearance analysis.

2 Results and discussion

The TG-DTA curve of sample show that weightlessness is observed from 70 °C to 500 °C, and the weightlessness disappeared and LaNiO_3 appeared from the temperature of 650 °C. The lowest peak temperature of cination is 214 °C.

The XRD patterns (Fig. 1) of dried gel calcined respectively show that the cination of dried gel experienced different decomposition mechanism when molar ratio 1:1:0.0 to 1:1:5.0. Pure perovskite LaNiO_3 is obtained when molar ratio 1:1:0.6. With the content of citrate increasing, content of complex ions of metal and citrate increased in further, cination temperature of dried gel decreased much. Cination temperature decreased from 360 °C (molar ratio 1:1:0.2) to 214 °C (molar ratio is 1:1:0.6).

The SEM pattern (800 °C, 2 h) of product show that LaNiO_3 is sheet and its size is irregular when the molar ratio is more than 1:1:1.0. While the content of citric acid excess the stoichiometric ratio, net LaNiO_3 is obtained. Uniformly nanoscaled LaNiO_3 bar is got when the proportion of lanthanum nitrate, nickel nitrate and citric acid is between 1:1:0.6 and 1:1:0.7.

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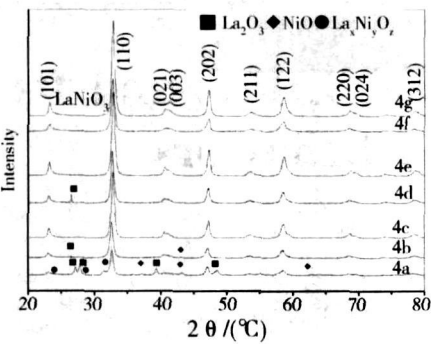


Fig 1 XRD spectra for samples of dried gel cination at 800 °C for 2 h respectively $\text{La}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, $\text{C}_6\text{H}_8\text{O}_7$ 4a=1:1:0.4b=1:1:0.24c=1:1:0.64d=1:1:0.84e=1:1:1.04f=1:1:3.04g=1:1:5.0 ■ La_2O_3 ◆ NiO ● LaNiO_3

3 Conclusion

Different molar ratios of H_3Cit to $\text{La}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_2$ had much influence on cination temperature of dried gel, oxide species and structure of cination products. Cination reactions are mainly affected for $\text{La}(\text{NO}_3)_3 \rightarrow \text{LaON} + \text{N}_2\text{O}$ when the molar ratio is low. Peak temperature of cinations is influenced for

$\text{LaNiCit} \rightarrow \text{NO} + \text{La}_2\text{O}_3 + \text{CO}_2$ when the molar ratio is high. The molar ratio of citric acid had much influence on the chemical components of complex. Perovskite LaNiO_3 is obtained when the molar ratio of $\text{La}(\text{NO}_3)_3$: $\text{Ni}(\text{NO}_3)_2$: $\text{C}_6\text{H}_8\text{O}_7$ are 1:1:0.6 and 1:1:1.0~1:1:5.0. Uniform nanoscaled LaNiO_3 bar is got when the proportion of lanthanum nitrate, nickel nitrate and citric acid is between 1:1:0.6 and 1:1:0.7.

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柠檬酸比对合成钙钛矿型 LaNiO_3 催化剂结构的影响

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摘要：以柠檬酸为配体采用溶胶-凝胶法合成了钙钛矿型双功能氧电极催化剂 LaNiO_3 。热重-差热 (TG-DTA)、X射线衍射 (XRD) 分析、电镜扫描 (SEM) 等表征结果表明：不同柠檬酸比对凝胶灰化、产物的结构和成分均有较大影响。当硝酸镧、硝酸镍、柠檬酸配比 1:1:0.6~1:1:0.7 时可制备出颗粒均匀的纳米棒状 LaNiO_3 。
关键词： LaNiO_3 ；溶胶-凝胶法；柠檬酸；钙钛矿型氧化物
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