

Improved Cellulose Adsorption Method for the Preparation of Perovskite Oxides with Large Specific Surface Area at Low Temperature

Zong Ping SHAO, Guang Tao LI, Guo Xing XIONG*, Wei Shen YANG

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O.Box 110, Dalian 116023

Abstract: Perovskite-type $\text{La}_{1-x}\text{Sr}_x\text{MO}_{3-\delta}$ ($x=0,0.1,0.2$, $\text{B}=\text{Co,Fe,Mn}$) oxides were prepared by pyrolysis of metal salt-(organic acid)-cellulose compound precursors. Low calcination temperatures, usually lower than 600°C , were needed. The specific surface area of the as-prepared oxides is higher than that prepared by the cellulose adsorption method, and is comparable to that prepared by sol-gel method. The effective organic acid could be EDTA acid, citric acid or DL-hydroxysuccinic acid, among them, EDTA acid is the best one.

Keywords: Perovskite, synthesis, cellulose, organic acid, surface area.

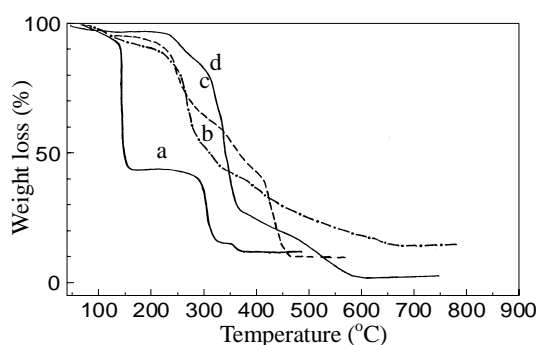
Wet chemical methods have lots of advantages over the traditional solid state reaction for the synthesis of mixed oxides¹. In this letter, we report the preparation of $\text{La}_{1-x}\text{Sr}_x\text{MO}_{3-\delta}$ ($x=0,0.1,0.2$, $\text{M}=\text{Co,Fe,Mn}$) functional oxide powders by improved cellulose adsorption method, *i.e.*, pyrolysis of metal salt(-organic acid)-cellulose compounds, which takes both the advantages of Pechini method (high surface area and low pyrolysis temperature) and cellulose adsorption method (simplicity).

Several metal nitrates (La, Sr, Co, Fe) and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were used as the metal precursors. The preparation of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, for example, was described as follows. Stoichiometric amounts of $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Mn}(\text{CH}_3\text{COO})_2$ were prepared into a mixed aqueous solution, then suitable amount of cellulose was added and impregnated in the resulting solution for a period of time. Such system was vibrated at 50°C for several hours to make the metal salts adsorbed on the cellulose surface strongly and homogeneously, followed by adding organic acid aqueous solution (mole ratio of total ions to acid is around 1.0:1.05), and vibrate again at 50°C for another several hours. The final system was dried at $60\text{--}80^\circ\text{C}$ to evaporate the water, and a solid precursor was obtained. The precursors were calcined in a muffle oven at the aimed temperature for 2h to obtain the final products.

The precursors were served to thermal analysis, which showed that all the cellulose-organic acid-metal salt precursors had similar thermal decomposition curves. **Figure 1** shows the TG curves of activated cellulose and different types of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ precursors. The weight loss went to balance around 440°C for cellulose-EDTA-metal salt precursor, 590°C for cellulose, 650°C for EDTA-metal salt precursor, and 400°C for

cellulose-metal salt precursor, which demonstrated that the introduction of cellulose could effectively lower the temperature needed for the burnout of organic compound in precursors. For metal-cellulose precursor, the pyrolysis took place mainly in two steps: the oxidation of C-O-C and CH₂-OH groups of cellulose and the reduction of NO₃⁻ at around 150°C, and the burnout of cellulose at around 290°C². But for cellulose-EDTA-metal salt precursor, the weight loss took place in the whole temperature range from 210°C to 440°C, which demonstrates the complexity of its pyrolysis mechanism.

Figure 1 TG curves of cellulose



a: Precursor of La_{0.8}Sr_{0.2}CoO₃ prepared by cellulose adsorption method,
 b: Cellulose,
 c, d: Precursors of La_{0.8}Sr_{0.2}CoO₃ prepared by EDTA complexing method and improved cellulose adsorption method (metal salt-EDTA-cellulose) respectively,
 air flow rate: 30ml/min, heating rate: 10°C/min

Figure 2 shows the XRD profiles of La_{0.8}Sr_{0.2}MnO₃ (LSM) cellulose-citric-metal salt precursor calcined at different temperatures for 2h. The calcined product of precursor was starting to crystallize into LSM at 500°C, and pure perovskite phase was formed at a calcination temperature higher than 550°C. The precursor crystallized into perovskite without any development of minor phase, which was indicative of the homogeneity of the cellulose-metal salt-citric precursors. Low calcination temperatures were needed for preparation of pure phase La_{1-x}Sr_xMO_{3-δ} (x=0, 0.1, 0.2, M=Co, Fe, Mn) oxide powders (**Figure 3**). For example, pure phase LaCoO₃ can be obtained by calcining the cellulose-citric-metal salt precursor at a temperature as low as 450°C, however, a calcining temperature higher than 1000°C was needed by solid state reaction, and calcination temperature higher than 600°C was needed by citric complexing method and poly (acrylic acid) sol-gel type method^{3,4}. The BET areas of the calcined products at 550°C were listed in **Table I**. The PSA of the powders prepared by this method were among 10-30m²/g, comparable to that prepared by sol-gel type complexing methods.

Figure 2. XRD profiles of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ precursor (cellulose-citric-metal salt compound) fired at various temperatures for 2h, for a: 400°C, b: 500°C, c: 550°C, d: 600°C

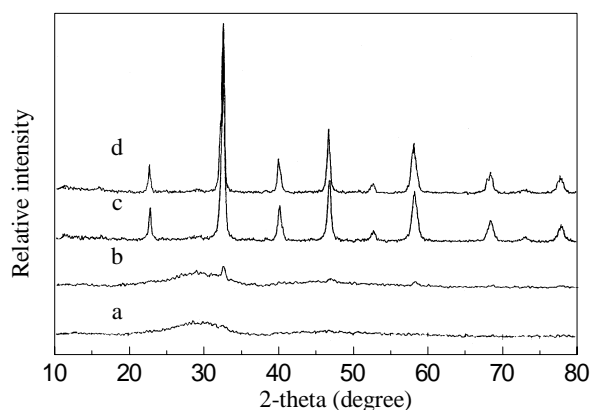


Figure 3. Phase composition of precursors (cellulose-citric-metal salt compounds) fired at various temperature for 2h for preparation of A: $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$, B: $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$, C: LaCoO_3 , D: $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$, E: $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$, F: LaFeO_3 , G: LaMnO_3 , H: $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$. The symbols represent for * : Perovskite plus amorphous phase, ■ : Perovskite, and □ : Amorphous phase

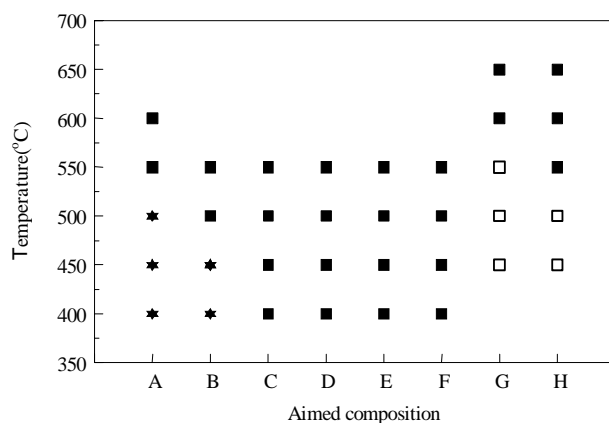


Table I Specific surface area (PSA) of $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ oxides prepared by pyrolysis of metal salt-citric-cellulose compounds at 550°C for 2h

Compound	LaCoO_3	LaFeO_3	LaMnO_3	$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	$\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$	$\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$
Cal-Temp. (°C)	450	450	600	550	540	450
PSA(m^2/g)	12.1	19.2	8.4	28.5	18.6	31.4

Table II The properties of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ powders prepared by pyrolysis of metal(-organic acid)-cellulose compounds

Acid	none	EDTA	Citric acid	Tartaric acid	HS acid
Cal-temp. ($^{\circ}\text{C}$)	500	500	540	500	500
PSA (m^2/g)	4.2	22.5	18.4	12.8	16.8
Cryst-size (nm)	19.6	22.4	22.4	35.6	11.8
Grain size (nm)	156	29	35	51	39

Solov'eva⁵ reported the synthesis of YSZ ultrafine powder by pyrolysis of metal-oxalate-cellulose compound at low temperatures. However, our results testified that it was ineffective to prepare above-mentioned compounds due to the coprecipitation of metal oxalate. It turns out that EDTA, citric acid and DL-hydroxysuccinic acid (HS acid) were recommendable as the organic acid. The physical properties of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ oxide prepared by pyrolysis of cellulose-(organic acid)-metal salt precursors with different organic acids was shown in **Table II**. The calcined product of precursor with EDTA as the acid had the highest PSA and finest crystallite size. Although pyrolysis of cellulose-metal compound was also effective to prepare LSCO at relatively low temperature (500°C)², the specific surface area is only about $4.2\text{m}^2\cdot\text{g}^{-1}$, lower than that prepared by EDTA complexing method⁶, and much lower than that prepared by the cellulose-EDTA-metal method. The new method was found also to be effective for preparation of other types composite oxides. The further investigation is just underway by our group.

The as-prepared powders were easily sintered to dense bodies. Relative density of *ca.* 98% of the theoretical density was obtained for the LSCO membrane sintered at 1250°C for 5h. Furthermore, SEM morphology showed that the grains of the membrane had a very narrow size distribution with a mean size of about $3.0\mu\text{m}$.

Acknowledgments

The authors gratefully acknowledge financial supports from the National Natural Science Foundation of China (Grant No. 59789201), the National Advanced Materials Committee of China (Grant No. 715-006-0122) and the Ministry of Science and Technology, China (Grant No. G1999022401).

References

1. C.D.Chandler, C.Roger, M.J.Hampden-Smith, *Chem.Rev.*, **1993**, 93, 1205.
2. Z.P.Shao, G.X.Xiong, W.S.Yang, *J.Inorganic.Mater.* (in Chinese), **2000**, 15(1), 123.
3. H.M.Zhang, Y.Teraoka, N.Yamazoe, *Chem.Lett.*, **1987**, 665.
4. H.Taguchi, H.Yoshioka, M.Nagao, *J.Mater.Sci.Lett.*, **1994**, 13, 891.
5. L.V.Solov'eva, I.A.Bashmakov, V.P.Novikov *et al.*, *Inorganic Mater.*, **1995**, 31, 1416.
6. Z.P.Shao, S.S.Sheng, G.X.Xiong *et al.*, *Functional Materials* (in Chinese), **1998**, 29, 1091.

Received 15 May 2000