

Rapid Chelatometric Determination of Chemical Composition of Lanthanum-Strontium-Manganate using Mixed Metallochromic Indicator

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ABSTRACT

A simple complexometric method for stepwise determination of lanthanum, strontium and manganese in Lanthanum-Strontium-Manganate (LSM) has been worked out. The method involves joint titration of the elements with EDTA at pH 10.0 followed by selective precipitation of strontium as sulphate from a homogenous solution involving displacement reaction between EDTA complex of strontium and $ZnSO_4$. The EDTA released from Sr-EDTA complex is the measure of strontium. In the same solution lanthanum is complexed with fluoride and EDTA released from La-EDTA complex is titrated with standard zinc solution and the equivalent concentration of lanthanum is calculated. The mass proportion of manganese is obtained after subtracting lanthanum and strontium from the joint titration of all the three elements.

The optimum conditions for precipitation of $SrSO_4$ and interferences due to various ions have also been studied. Complexometric analysis results obtained for La, Sr and Mn in LSM samples compare favorably with those obtained by modern instrumental Inductively Coupled Plasma Atomic Emission Spectrometric (ICP AES) method.

Keywords: lanthanum-strontium-manganate (LSM), complexometric method, mixed indicator

INTRODUCTION

High-temperature solid oxide fuel cell (SOFC) is the most efficient and environment friendly energy conversion technology to generate electricity from fuels such as hydrogen and natural gas as compared to the traditional thermal power generation plants. In the last 20-30 years, there has been significant progress in the materials development and stack technologies in SOFC. Among the electrode materials, lanthanum strontium manganite (LSM) of composition $Sr_xLa_{1-x}MnO_3$ perovskites, till today, are the most investigated and probably the most important electrode materials in SOFC¹. The physicochemical properties of the material vary in relation to the composition ($0.1 \leq x \leq 0.5$). The performance of LSM cathode is sensitive to its chemical composition and any change in composition of the material will impair its electrical characteristics.

Considering the excellent and extensive application of LSM, a reliable and rapid method for the determination of chemical composition of LSM is

often essential. Sophisticated instruments like ICP-AES and ICP-MS² are utilized for chemical analysis of LSM because they are more time saving and have greater accuracy. Because of the expensive investment for such instrumentation, there is a need for a simple, rapid and accurate titration method like complexometry to determine the chemical composition of LSM. It is important especially to those laboratories where there are difficulties in purchasing instruments like ICP-AES or ICP-MS.

Complexometric titrations are widely used for the determination of metal ions. Usually, only one component is titrated at a time. In some cases, two or three components can be determined simultaneously by means of changing the pH of the test solution with addition of different buffers or masking agents to the solution³⁻⁵.

The aim of this work is to present a simple, rapid and accurate complexometric method for the determination of chemical composition of lanthanum-strontium-manganate SOFC material.

At first an artificial mixtures similar to LSM were prepared and lanthanum, strontium and manganese were determined in the mixture by visual end point detection using metallochromic indicators applying the proposed method. The method was then applied for the analysis of actual samples.

EXPERIMENTAL

All reagents, unless specified otherwise, were of analytical reagent grade. De-ionized water (18 mega ohm resistivity) prepared from the Millipore milli-Q water purification system, USA, was used throughout.

Standard Lanthanum solution, 0.02M

2.78 g pure lanthanum metal (99.99 %) was dissolved in 20 ml hot dilute nitric acid (1:1), boiled, cooled and diluted to 1 liter.

Standard Strontium solution, 0.01M

2.1162 g pure strontium nitrate (99.99 %) was dissolved in 20 ml hot dilute nitric acid (1:1), boiled, cooled and diluted to 1 liter. boiled, cooled and diluted to 1 liter.

Standard Manganese solution, 0.01M

0.55 g pure manganese metal (99.98 %) was dissolved in 20 ml hot dilute nitric acid (1:1), boiled, cooled and diluted to 1 liter.

Standard Zinc solution, 0.01M

0.6539 g pure zinc metal (99.99 %) was dissolved in 20 ml hot dilute nitric acid (1:1), boiled, cooled and diluted to 1 liter.

Zinc sulphate solution, 0.01M

1.6139 g zinc sulphate was dissolved in water and diluted to 1 liter.

Standard EDTA solution, 0.01M

3.744g of the disodium salt of EDTA was dissolved in water and diluted to 1 liter. The solution was standardized with standard 0.01M zinc solution using mixed indicator at pH 10.0.

Buffer solution (pH 10.0)

67.5 gm of ammonium chloride was dissolved in 250 ml water and 57.0 ml of ammonia solution (sp. gr. 0.91) was added, diluted to 1 litre.

Mixed indicator solution

Eriochrome Black T (0.03g), titan yellow (0.04g) and naphthal green B (0.01g) were dissolved in 25 ml triethanolamine.

Hydroxyl amine hydrochloride and Ammonium fluoride were used.

Preparation of sample solution

A 0.5g of the dried ($105^{\circ} - 110^{\circ}\text{C}$) sample was accurately weighed in a 250 ml glass beaker and 50 ml of distilled water was added. Then 10 ml of concentrated hydrochloric acid was added. The solution was kept boiling for 10 minutes to digest the sample. The solution was cooled and diluted to 250 ml using a volumetric flask.

Procedure

A portion of solution containing lanthanum (5-25 mg La), strontium (2-10 mg Sr) and manganese (2.5-12.5 mg Mn) was transferred to a 250 ml conical flasks. Solution was diluted to about 100 ml with distilled water. About 0.5 gm of hydroxyl amine hydrochloride was added followed by dilute ammonia solution (1+4) drop-wise until the content of the flask had the smell of ammonia. About 10 to 15 ml of buffer solution (pH 10.0) was added and the mixture was titrated with 0.1 M EDTA solution in the presence of 10-12 drops of mixed indicator until a sharp change of color from pink to green was obtained. Let the titre value is 'A' ml of EDTA.

Determination of strontium

The above solution was heated on a hot plate to $50-60^{\circ}\text{C}$ and 10 ml of zinc sulphate solution was added followed by the addition of 5-6 gm of potassium sulphate. The solution was boiled for 10 mins in order to precipitate strontium sulphate. The solution was cooled to room temperature. About 10 ml of buffer solution (pH 10.0) and 20 ml of absolute ethanol were added. Excess zinc solution was titrated with EDTA to the sharp green end point. Let the titre value is 'B' ml of EDTA. 10 ml of zinc sulphate solution was titrated separately with EDTA at pH 10.0. Let the titre value is 'C' ml of EDTA.

$$\text{Then, Sr (mg)} = (C - B) \times f$$

where, f is the equivalent of strontium in mg/ml of EDTA solution.

Determination of lanthanum

After determination of strontium, about 1 to 2 g of NH_4F was added to the same solution. The solution was boiled for 10 minutes. The solution was cooled and 10 ml of buffer pH 10.0 was added. The released EDTA was titrated with standard zinc solution. End point was green to pink. Let the titre value is 'D' ml of zinc solution. 10 ml of standard zinc solution was titrated with EDTA at pH 10.0 separately.

$$\text{Then, La (mg)} = E \times g$$

where, 'E' is the volume of EDTA equivalent to volume 'D' of standard zinc solution and g is equivalent of La in mg/ml of EDTA.

Determination of manganese

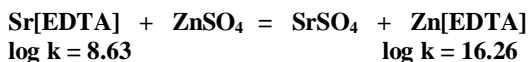
$$\text{Mn (mg)} = [A - \{ (C - B) + E \}] \times h$$

Where, h is the equivalent of Mn in mg/ml of EDTA solution.

RESULTS AND DISCUSSION

Various methods based on direct and back titrations of lanthanum, strontium and manganese with EDTA are reported in the literature^{6,7}. When these elements are present together they are co-titrated and therefore prior separation of individual element is essential for their determination. Ushakova et.al⁸ described a complexometric method for chemical analysis of LSM which involve precipitation, separation and repeated titrations. The procedure is found to be rigorous and lengthy.

The present work describes a method in which lanthanum, strontium and manganese are complexed by titration with EDTA at pH 10.0 in the presence of mixed indicator. Strontium is then precipitated as sulphate at the same pH from a homogeneous solution by displacement reaction with a known (excess) solution of zinc sulphate



Higher value of stability constant of Zn-EDTA complex compared to that of strontium show that the reaction is stable. The conditional stability constants of Sr-EDTA and Zn-EDTA are found to be 5.28 and 12.41 respectively at pH 10.0. Since the conditional stability constant of Zn-EDTA is greater than that of Sr-EDTA by 7 units, the conditions for successful replacement and precipitation reaction is fulfilled. The excess amount of zinc ion is then titrated with EDTA solution. Strontium is calculated from the equivalent amount of zinc consumed during displacement reaction. Sulphate ion plays an important role in the precipitation of strontium from homogeneous solution after its replacement reaction with zinc sulphate. In the present study, it was observed that the precipitation of strontium is increased with the increase of excess of sulphate ion concentration. For quantitative precipitation of strontium sulphate, however, a large excess of sulphate ions (more than 0.25M) is preferable.

Temperature is also an important parameter to be optimized. Quantitative precipitation of strontium sulphate at room temperature takes too long a time while on increasing the temperature of the solution, precipitation of strontium sulphate increases. The

quantitative precipitation of strontium sulphate requires the solution to be boiling.

The metallochromic indicator Eriochrome Black T is used in the direct titration of lanthanum, strontium and manganese with EDTA at pH 10.0. However, the end point from red to blue is not sharp and is sometimes confusing. In an attempt to improve the end point by producing a change from red to green, addition of yellow dyes⁹⁻¹¹ have been reported. In the present study we used Titan Yellow in conjunction with Eriochrome Black T and Naphthol green B and this mixed indicator gave a sharp change from pink to green in the titration of lanthanum, strontium and manganese with EDTA. The end point during the titration of excess of zinc with EDTA after precipitation of SrSO₄, in absence of absolute ethanol, however, reverted from green to pink within a few seconds, probably as a result of the greater solubility of strontium sulphate. The addition of 10 to 15 ml of absolute ethanol was necessary to reduce the solubility of SrSO₄.

For quantitative de-masking of lanthanum from its EDTA complex, ammonium fluoride was found to be suitable. Thus on reaction of La-EDTA complex with NH₄F, more stable lanthanum fluoride was formed and liberated EDTA was titrated with standard zinc solution. The reaction is found to be slow at room temperature. However, the rate of reaction increases with the increase in temperature and quantitative formation of lanthanum fluoride requires the solution to be boiling. The results obtained with synthetic solution are shown in Table 1.

Iron has strong interference with the procedure. The end point of titration is affected and the color of the indicator is faded. The interference due to iron is eliminated by precipitating iron with hexamine at pH 6.0 during preparation of sample solution. Cu, Ni and Co interfered by inactivating the indicator and those interferences were eliminated by masking with 1,10-orthophenanthroline (shown in Table 2). Interference due to Al and Ti were eliminated by masking with triethanolamine.

The method has been successfully applied to the determination of lanthanum, strontium and manganese present in lanthanum-strontium-manganate samples. Results (Table 3) obtained for La, Sr and Mn in some LSM samples compare favorably with those obtained by modern instrumental method like Inductively Coupled Plasma Atomic Emission Spectrometric (ICP AES) method.

Table 1: Precision and accuracy of the method

Amount taken in mg			Amount found ^a in mg			Coeff. Of variation (%)			Relative error (%)			t _{calculated} ^b		
La	Sr	Mn	La	Sr	Mn	La	Sr	Mn	La	Sr	Mn	La	Sr	Mn
25.00	2.00	2.50	24.99	1.99	2.49	0.08	1.00	0.80	-0.04	-0.50	-0.40	1.11	1.12	1.12
20.00	4.00	5.00	20.02	4.01	5.01	0.15	0.50	0.40	+0.10	+0.25	+0.20	1.49	1.11	1.11
15.00	6.00	7.50	14.99	5.98	7.51	0.20	0.67	0.40	-0.06	-0.33	+0.13	0.75	1.11	0.75
10.00	8.00	10.00	10.01	7.98	9.99	0.40	0.63	0.30	+0.10	-0.25	-0.10	0.56	0.89	0.74
5.00	10.00	12.50	4.99	10.01	12.51	0.60	0.30	0.32	-0.20	+0.10	+0.08	0.75	0.75	0.56

a. Average of five determinations.

b. Calculated t-value for 4 degrees of freedom at p (0.95) is 2.78.

Table 2: Determination of Lanthanum, strontium and manganese in presence of various ions

La taken = 5.00 mg, Sr taken = 2.00 mg, Mn taken = 2.50 mg				
Ion	Added, mg	La found, mg	Sr found, mg	Mn found, mg
Fe	8.50	4.97	2.01	2.48
Al	20.00	5.01	1.98	2.51
Ti	2.00	5.03	2.05	2.53
Ni	20.00	4.98	2.03	2.49
Cu	30.00	5.02	2.01	2.52
Co	20.00	5.04	1.97	2.47

Table 3: Results of chemical analysis of Lanthanum-Strontium-Manganate (P = 0.95, t_p^s = 2.78)*

Test Method	Component	Calculated mass, %	X ± tS/√n, %	S	S _r , %
ICP-AES	La	35.00	35.03 ± 0.12	0.098	0.28
	Sr	14.00	14.01 ± 0.15	0.120	0.85
	Mn	25.00	25.02 ± 0.17	0.137	0.55
Complexometric	La	35.00	35.02 ± 0.39	0.310	0.89
	Sr	14.00	14.02 ± 0.36	0.291	2.08
	Mn	25.00	25.01 ± 0.30	0.242	0.97

*P – proof probability,

t_p^s - tabular Student coefficient (for 5 determinations),

X = mean of five determinations, S = standard deviation,

S_r = relative standard deviation.

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