The element content determination of LiCo_xNi_yMn_zO₂ by inductively coupled plasma atomic emission spectrometric method

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Abstract. The contents of Ni, Co, Mn and Li in $LiCo_xNi_yMn_zO_2$ cathode material were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) method. The samples were dissolved in aqua regia. The analytical spectral line for Ni, Co, Mn and Li was 232.0, 237.8, 279.4 and 610.3nm, respectively. The concentration of each element was linearly related to the emission intensity in the chosen range of concentration. The detection limit was 0.0005% to 0.001% while the addition standard recovery was 99%~101%. The ICP-AES method was applied to the element content determination of standard samples. The results were essentially in agreement with the certified values and the relative standard deviation (n=6) was between 0.85% and1.03%.

Introduction

Lithium ion battery has been widely used in portable electronic products, and it's also considered to be the most promising power source in the near future for electric vehicles and hybrid electric vehicles ^[1]. At present, the scientists are committed to the development of such cathode materials with high capacity, low cost and high safety ^[2]. LiCo_xNi_yMn_zO₂ was developed from LiCoO₂ by using Ni and Mn to replace part of Co in the original cobalt acid lithium layered structure. As the amount of cobalt reduced, the cost was reduced and the energy density was improved. LiCo_xNi_yMn_zO₂ also has good thermal stability and wide charge and discharge voltage which makes it to be the ideal cathode material to fulfill the requirement of power battery ^[3,4]. Its electrochemical properties are determined by the content ratio of Ni, Co, Mn in LiCo_xNi_yMn_zO₂. The inductively coupled plasma atomic emission spectrometry (ICP-AES) method was widely applied to element content determination due to its low detection limit, wide dynamic range, high accuracy and little matrix effect ^[5-9]. In this paper, the contents of Ni, Co, Mn and Li in LiCo_xNi_yMn_zO₂ were determined by ICP-AES method. The samples were dissolved in aqua regia. The selection spectrometry of Ni, Co, Mn and Li was 232.0, 237.8, 279.4 and 610.3nm, respectively. It turns out that the ICP-AES detection method of LiCo_xNi_yMn_zO₂ is simple, fast and accurate.

Experiment

Instrument and reagent.The ICAP6300 inductively coupled plasma atomic emission spectrometry (ICP-AES) was used. The selection spectrometry line for Ni, Co, Mn and Li was 232.0, 237.8, 279.4 and 610.3nm, respectively. The high frequency generator power in resection is 1150W. The flow rates is $0.50L \cdot \min^{-1}$ and carrier gas flux is $0.75L \cdot \min^{-1}$. The peristaltic pump assembly speed was set at 50 R·min⁻¹. The integral time is 15s and observation height is15mm. Hydrochloric acid and nitric acid are both guarantee reagent, resistivity of de-ionized water is 18M $\Omega \cdot cm$. 0.1000g powder sample was dissolved completely by 10ml aqua regia in the beaker. After cooling down, the solution was transferred to a 200ml volumetric flask and diluted to the volume with water. Shake the bottles before using. The atomic emission spectrometry of the sample as well as the blank reagent was tested by ICP-AES.

Preparation of nickel standard solution (1.000g·L⁻¹): 0.5000g spectroscopically pure Ni was

mixed with 20ml nitric acid(1+1), heated and dissolved, and then diluted to 500ml.

Preparation of cobalt standard solution($1.000g\cdot L^{-1}$): 0.5000g spectroscopically pure Co was mixed with 30ml hydrochloric acid(1+1), heated and dissolved, and then diluted to 500ml.

Preparation of manganese standard solution $(1.000g\cdot L^{-1})$: 1.000g spectroscopically pure Mn was mixed with 20ml nitric acid(1+1), heated and dissolved, and then diluted to 1000ml.

Preparation of lithium standard solution($1.000g\cdot L^{-1}$):1.0648g spectroscopically pure Li₂CO₃ was mixed with 30ml hydrochloric acid(1+1), heated and dissolved, and then diluted to 1000ml.

Results and Discussion

Selection of analytical spectral lines

Selection of analytical spectral lines depends on the level of sensitivity. Lines with less spectral interferences and high sensitivity will be selected as analytical spectral lines. Primary lines (221.6nm、232.0nm for Ni, 228.6nm、230.7nm、237.8nm for Co, 191.5nm、257.6nm、279.4nm、348.291nm for Mn, 610.3nm、670.7nm for Li) were selected as spectrum library recommended. After scanning the primary lines, those lines with good peak shape and light spectral interference which could be easily eliminated were kept. The eventually selected lines for Ni, Co, Mn and Li were 232.003nm, 237.862nm, 279.482nm and 610.362nm, respectively.

Optimization of Working conditions of the instrument

The optimization was taken by changing the parameters of the instrument (including peristaltic pump assembly speed, flow rates and RF power etc.) to reach the right levels with maximum intensity and minimum noise. RF power was set at 950W, 1050W, 1150W and 1250W. Atomization pressure was set at $0.6L \cdot \min^{-1}$, $0.7L \cdot \min^{-1}$, $0.8L \cdot \min^{-1}$ and $0.9L \cdot \min^{-1}$. Peristaltic pump assembly speed was set at $20R \cdot \min^{-1}$, $30R \cdot \min^{-1}$, $40 R \cdot \min^{-1}$ and $50 R \cdot \min^{-1}$. Observation height was set at 8 mm, 10mm, 15mm and 20mm. Working conditions were optimized according to orthogonal experiment results. The best instrument working conditions include 1150W of RF power, $0.50L \cdot \min^{-1}$ of flow rates, $0.75L \cdot \min^{-1}$ of carrier gas flux, 50 R \cdot min^{-1} of peristaltic pump assembly speed, 15s integral time and 15mm observation height.

Working curves and the detection limit

A certain volume of $1.000g \cdot L^{-1}$ standard solution(1, 5, 10, 25ml for Ni, Co, Mn and 1, 2, 5, 10ml for Li) was transferred to a 100ml volumetric flask respectively, added by 5ml aqua regia, and then diluted to the volume with water. The Ni, Co, Mn and Li mixture standard solution with different concentration was obtained shown in Table 1.

No.	Std 0	Std 1	Std 2	Std 3	Std 4
ρ(Ni)	0.00	10.00	50.00	100.00	250.00
ρ(Co)	0.00	10.00	50.00	100.00	250.00
ρ(Mn)	0.00	10.00	50.00	100.00	250.00
_ρ(Li)	0.00	10.00	20.00	50.00	100.00

Table 1 Concentration of Ni, Co, Mn and Li in mixture standard solution (µg·ml⁻¹)

The calibration curves were obtained by taking the concentration of Ni, Co, Mn and Li as the X-axis and the corresponding emission intensity as the Y-axis. The calibration curve regression equations, linear ranges and correlation coefficients are shown in Table 2. The correlation coefficients of the calibration curve are all above 0.999 as shown in Table 2. Determination of blank solution was repeated 10 times. The detection limit was defined as 3 times the standard deviation of the determination results. The detection limit of Ni, Co, Mn and Li was respectively 0.0008%, 0.001%, 0.0005% and 0.0005%.

Element	Linear regression equation	Linear range(µg⋅ml ⁻¹)	Correlation coefficient
Ni	y=251.8994x+0.0897	0~250	0.9999
Co	y=881.3212x-00.7329	0~250	0.9998
Mn	y=1636.1931x-0.2249	0~250	0.9997
Li	y=55136.1964x-866.288	0~100	0.9992

Table 2 Regression equation and correlation coefficient

Precision

The test for precision of Ni, Co, Mn and Li was taken under the best working conditions of the instrument. 100μ g/ml Ni, 100μ g/ml Co, 100μ g/ml Mn and 50μ g/ml Li were used as Standard solutions. Each was determined for 6 times. As the results shown in Table 3, the determination values were in agreement with the certified values and the relative standard deviation of each element was between 0.85% and 1.03%.

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Element	Certified $(\mu g \cdot ml^{-1})$	Found $(\mu g \cdot ml^{-1})$	RSD/%
Ni	100.00	100.06	0.85
Co	100.00	100.09	1.03
Mn	100.00	100.00	1.00
Li	50.00	49.85	0.97

Table 3 Results of test for precision (n=6)

Recovery test

The results for recovery were shown in Table 4. As can be seen, the recovery rates for Ni, Co, Mn and Li is100.2, 101.7, 99.1 and 101.9, respectively. And the relative standard deviation is from 0.54% to 1.33%. The satisfactory results of the experiment demonstrated that the ICP-AES method is suitable for $LiCo_xNi_yMn_zO_2$ cathode material.

Element	Found w /%	Addition w /%	Total found w /%	Recovery/%	RSD/%
Ni	30.43	30.00	60.58	100.2	0.54
Co	12.45	15.00	27.92	101.7	1.02
Mn	16.62	18.00	34.32	99.1	0.87
Li	6.99	7.00	14.26	101.9	1.33

Table 4 Results of test for recovery (n=6)

Summary

The contents of Ni, Co, Mn and Li in $LiCo_xNi_yMn_zO_2$ cathode material were determined by ICP-AES method. The analytical spectral line for Ni, Co, Mn and Li was 232.0, 237.8, 279.4 and 610.3nm, respectively. The correlation coefficients of the calibration curve are above 0.999. The detection limit was 0.0005% to 0.001% while the addition standard recovery was between 99% and 101%. It turns out that ICP-AES is a scientific and effective method to the determination of Ni, Co, Mn and Li in $LiCo_xNi_yMn_zO_2$ cathode material.

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