Prediction of Decomposition Temperature for Lanthanide Complexes Involving Cyclopentadienyl and Benzohydroxamic Acid Ligand by ANNs

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The decomposition temperatures of the lanthanide organic complexes (η^5-C_5H_5)$_2$Ln(C_6H_5CONHO) involving cyclopentadienyl and benzohydroxamic acid ligands were calculated and predicted by the model based on ANNs (artificial neural networks) method. The comparison was carried out between results from ANNs method and traditional regression method. It is proved that ANNs could be used more efficiently for the prediction of decomposition temperature of lanthanide organic complexes.

Keywords rare earth organometallic, artificial neural network, decomposition temperature

Introduction

Since Wilkinson and Birmingham[1,2] for the first time synthesized cyclopentadienyl rare earth compounds with stable chemical properties in 1954, the synthesis and preparation of rare earth organometallic compounds have become an attractive research field. As the potentially practical material and useful chemical substance such as available high performance catalyst, some physical properties of rare earth organometallic compounds should be concerned. In preparation of rare earth organometallic compounds, a lot of work has been done in our group and this work deals with the temperature of decomposition of these organometallic compounds by means of ANNs (artificial neural networks) and experiments. In recent years, ANNs have been used as a useful tool for the prediction of some properties of compounds, such as the successful prediction of enthalpy of fusion of rare earth halides.[3,4] The advantages of ANNs approach make it easy to deal with non-linear and more complicated problems. Moreover, the relations applied in ANNs among micro-structural parameters and the macro-physical properties are not required in advance, and it is not necessary to give some prior assumption and to know available information mechanismically. The rare earth organometallic compounds studied here are lanthanide complexes involving cyclopentadienyl and benzohydroxamic acid ligands, *i.e.*, (η^5-C_5H_5)$_2$Ln(C_6H_5CONHO). The temperatures of decomposition of seventeen lanthanide complexes were given here among which seven were measured in this work.

Experimental

The lanthanide complexes were prepared under purified Ar by using Schlenk techniques.[5] THF and *n*-hexane were refluxed and distilled over the sodium ketyl of benzophenone under Ar before use. The elemental analysis data for C, H and N were obtained on a Carlo Erba-1106 analyzer. IR spectra were recorded on a Perkin-Elmer 983 (G) spectrometer. MS spectra were obtained on an HP 5989A mass spectrometer. The analysis of Ln was conducted with published method, and tricyclopentadienyl rare earth compounds and benzohydroxamic acid were prepared by the reported method.[6] Finally the temperatures of

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decomposition for seven complexes were determined carefully in sealed argon-filled capillaries. The temperature of decomposition and the elemental analyses data are listed in Table 1. Data in parentheses in Table 1 are calculated according to molecular formula.

Network outline

A three-layered with one hidden layer back-propagation network was employed in this work. Each neuron in the input layer is completely interconnected with all neurons in the hidden layer, which are completely interconnected with the neuron in the output layer. Each connection has a weight associated with it, indicating the connection strength and being modulated by a certain learning calculus. And the bias was used to act to each neuron in the hidden and output layers.

To predicate the temperature of decomposition directly, two sorts of transfer functions were used, which are hyperbolic tangent sigmoid and lineal functions.

$$y = b_2 + \sum_{j=1}^{M} w_{2j} \frac{2}{1 + e^{-2(\sum_{i}^{m} w_{1ij} x_i + b_{1j})}} - 1 \qquad (1)$$

$$i = 1, 2, \cdots, m; \; j = 1, 2, \cdots, M$$

where m is the number of neuron in input layer, M the number of neuron in hidden layer, w_{1ij} the weight of the connection between the ith and jth neurons, w_{2j} the weight of the connection between the jth neuron in the hidden layer and the output neuron if there is only one output neuron, x_i the input of the ith input neuron, b_{1j} the bias of the jth neuron in hidden layer, b_2 the bias of the output neuron and y the output. The ANNs of this work involve only one output neuron. As the lineal function was used for output calculation, y can be any values not only within the $[-1,1]$ range.

Network training

There have been several methods for training a network. The weights and biases are modulated to the minimum summation of square errors through the continuous modulation of weights and biases in the steepest degressive direction of summation of square errors in the original BP learning method. This convergent speed of the original method is very slow. The momentum is introduced into learning process to become the modified method. The modified method uses the momentum to adjust the weights' variation from the previous layer. The Levenberg-Marquardt method calculates the derivative of errors against weights and is more speedy and efficient than the above two methods.[7]

Table 1 Temperature of decomposition and elemental composition of some complexes

Complex	Color	Decomp. temp. (℃)	Yield (%)	Found (calcd, %)			
				Ln	C	H	N
Pr	Yellow	121	32	33.40 (34.42)	49.16 (50.14)	3.23 (3.90)	4.05 (3.44)
Gd	Earth yellow	124	40	36.10 (36.83)	47.63 (48.20)	3.10 (3.81)	3.80 (3.31)
Dy	Yellow	146	50	36.95 (37.90)	46.82 (47.61)	3.11 (3.76)	3.70 (3.26)
Ho	Pale yellow	142	58	37.53 (38.42)	46.82 (47.35)	3.07 (3.74)	3.67 (3.23)
Er	Pink	155	60	37.79 (38.58)	46.18 (47.09)	3.69 (3.72)	3.06 (3.23)
Tm	White	156	63	38.02 (38.31)	46.15 (46.91)	3.52 (3.70)	3.30 (3.21)
Yb	Yellow	158	68	38.74 (39.38)	45.94 (46.47)	3.12 (3.76)	3.40 (3.20)

Network input and output

Since the organic group in this work is the same, the influence on the physical properties of rare earth organometallic compounds under study should mainly be considered from rare earth. The interaction of static electricity between rare earth element and organic group was supposed to be negligible. So the radius of rare earth was selected as the input vector by considering dimensional effect. Evidently the output in this case is some value related to the temperature of decomposition. As the lineal function is used in the ANNs for the second transfer one, the temperature of decomposition is read directly. Seven of rare earth organometallic compounds were synthesized and the measured temperature of decomposition for each one was used as target vector for training the network. Table 2 lists the radius values for input neurons and the temperatures of decomposition both from the experiments and the prediction.

Table 2 Radii of rare earth metals and temperatures of decomposition of rare earth organometallic compounds (ANNs)

Rare earth metal	Radius (nm)	Expt. decomp. temp. (℃)	Calcd decomp. temp. (℃)
Y	0.104	–	145.0
Sc	0.0885	–	190.3
La	0.1172	–	111.2
Ce	0.115	–	112.2
Pr	0.113	121	121.0
Nd	0.1123	–	123.0
Pm	0.111	–	123.9
Sm	0.1098	–	124.0
Eu	0.1087	–	124.0
Gd	0.1078	124	124.0
Tb	0.1063	–	125.4
Dy	0.1052	146	146.0
Ho	0.1041	142	142.0
Er	0.103	155	155.0
Tm	0.102	156	156.1
Yb	0.1008	158	158.0
Lu	0.1001	–	160.1

Network parameters

In the trainings, one sample among seven was left for testing the model. After several trials the best result was selected. The parameters of network from training such as weight matrix compose the predictive model. By using the network parameters together with Eq.(1) a program was made for the prediction of the temperature of decomposition. The network parameters are listed in Tables 3a—3d.

Prediction and comparison between ANNs *and regressions*

The leave-one-out method was used when training the networks. Fig. 1 shows the trend of sum-squared error on training set. To prove that ANNs are more reliable especially in this work, several regressive analyses were carried out, which used full of samples. Some prediction data from polynomial regressions near to light rare earth are not shown in Fig. 2 since the data are out of the range of temperature plotted in Fig. 1. The results of comparison for training set from different methods are listed in Table 4.

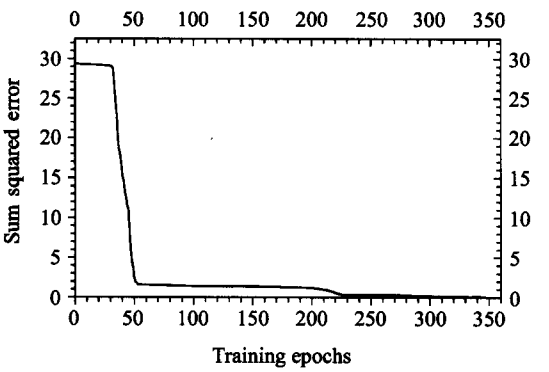

Fig. 1 Trend of sum-squared error on the training set.

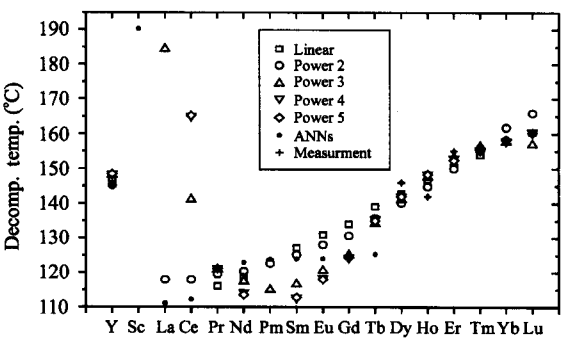

Fig. 2 Temperature of decomposition from measurement and prediction.

Table 3a Connection weights between the input and the hidden layer

W_{11}	W_{12}	W_{13}	W_{14}	W_{15}	W_{16}	W_{17}	W_{18}
-89.5520	99.8637	-98.3037	-171.2458	-38.4050	248.9223	83.8975	99.9557

Table 3b Biases for the hidden layer

B_{11}	B_{12}	B_{13}	B_{14}	B_{15}	B_{16}	B_{17}	B_{18}
101.7917	-93.3074	90.6843	179.5069	37.2308	-260.9636	-104.8283	-87.9604

Table 3c Connection weights between the hidden layer and output layer

W_{21}	W_{22}	W_{23}	W_{24}	W_{25}	W_{26}	W_{27}	W_{28}
6.4150	5.8879	-10.9026	116.9350	32.6086	101.5358	-9.7537	-7.3262

Table 3d Bias for the output layer

B_2
146.3547

Table 4 Comparison of relative error for training set from different methods

Rare earth	NNs (× 100)	Power 1 (× 100)	Power 2 (× 100)	Power 3 (× 100)	Power 4 (× 100)	Power 5 (× 100)
Pr	0.00	-4.00	-1.20	-0.06	0.21	0.17
Gd	0.00	8.05	5.38	0.90	0.20	0.26
Dy	0.01	-2.12	-4.07	-3.34	-2.74	-2.76
Ho	0.01	3.29	1.98	3.97	4.49	4.39
Er	0.03	-2.94	3.22	-1.26	-1.38	-1.73
Tm	0.01	-1.37	-0.56	0.26	-0.48	-0.39
Yb	0.01	-0.01	2.40	-0.13	-0.08	0.22

Conclusion

The relation between the micro-parameters and macro-properties for a substance is always of importance. ANNs are more efficient for the prediction of the temperatures of decomposition of the rare earth organometallics than the conventional algorithm since the relation is a completely nonlinear and complicated. Some more work about the temperatures of decomposition of the rare earth organometallic compounds with other organic groups will be done in series.

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