FREE RADICAL CHARACTERISTICS AND CLASSIFICATION OF COALS AND ROCKS USING ELECTRON SPIN RESONANCE SPECTROSCOPY**

Shuguang Miao[1,2,3], Xiaowen Liu[1,3*]

[1] *School of Information and Control Engineering, China University of Mining and Technology, Xuzhou, 221008, China*
[2] *School of Physics and Electronic Information, Huaibei Normal University, Huaibei, 235000, China*
[3] *IOT Perception Mine Research Center, China University of Mining and Technology, Xuzhou, 221008, China; e-mail:liuxiaowencumt@163.com*

Coal-rock interface recognition is one of the key unaddressed problems in unmanned mining, so a novel method for it is proposed. Firstly, electron spin resonance (ESR) is used to directly measure 10 kinds of coals/rocks common in China. Secondly, the free radical characteristics of different particle coals/rocks such as the Lande factor g, line width ΔH, and the concentration of the free radical Ng in the X-band ESR are studied. Lastly, the statistical classifier method of support-vector machine is employed to build a classification model with the input of the parameters of the ESR absorption spectra. Based on the ESR-SVM model, the recognition rate of coals/rocks reaches 100%, the recognition rate of different coals reaches 100%, and the recognition rate of different bituminous coals reaches 88.3%. The experimental results demonstrate that the proposed method is fast, stable, and accurate for the detection of the coal-rock interface and can be a promising tool for the classification of different coals.

Keywords: *coal-rock interface, electron spin resonance, free radical.*

СВОБОДНОРАДИКАЛЬНЫЕ ХАРАКТЕРИСТИКИ И КЛАССИФИКАЦИЯ УГЛЕЙ И ГОРНЫХ ПОРОД МЕТОДОМ ЭЛЕКТРОННОЙ ПАРАМАГНИТНОЙ РЕЗОНАНСНОЙ СПЕКТРОСКОПИИ

S. G. Miao[1,2,3], X. W. Liu[1,3*]

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[1] *Школа информационной и управляющей инженерии, Китайский горно-технический университет, Сюйчжоу 221008, Китай*
[2] *Школа физики и электронной информации, Хуайбэйский педагогический университет, Хуайбэй, Китай*
[3] *Китайский горно-технический университет, Сюйчжоу, 221008, Китай; e-mail: liuxiaowencumt@163.com*

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Предлагается метод распознавания поверхности угольных горных пород в условиях автоматизированного горнодобывающего процесса. Для определения свойств десяти видов угля, которые встречаются в Китае, используется электронный парамагнитный резонанс (ЭПР). Изучены свободнорадикальные характеристики частиц различных угольных пород: фактор Ланда g, ширина линии ΔH и концентрация свободных радикалов Ng в X-полосе ЭПР. Для построения классификационной модели, предполагающей введение параметров спектров поглощения ЭПР, используются статистические методы. На основе данной модели скорость распознавания угольных горных пород достигает 100%, различных углей 100%, битуминозных углей 88.3%.

Ключевые слова: *поверхность угольной породы, электронный парамагнитный резонанс, свободный радикал.*

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Introduction. China's energy resources are characterized by lack of oil and gas, but its coal resources are relatively plentiful. Therefore, coal is determined as the primary energy in China and it will play a major role in China's energy consumption for a long time in the future. However, with the increase in coal mining depth, some significant challenges arise, such as gas explosion, rock burst, collapse, water inrush, and other potential geological disasters [1–3]. In order to prevent these, it is necessary to reduce the number of miners through automatization. In other words, it is gradually becoming possible to achieve the goal of unmanned mining by means of remote-control fully mechanized coal mining equipment, which helps to increase the extraction rate of coal resources [4]. In addition, it can decrease the number of workers. However, coal-rock interface recognition is still a key unaddressed problem. Therefore, a noncontact ahead-looking device/sensor is needed, which can quickly and accurately distinguish the cutting state of the coal or rock.

At present, research on coal-rock recognition is a hot topic, and a series of technical methods has arisen. Bessinger and Nelson [5] measured the remnant roof coal thickness by passive gamma ray instruments in coal mines, but this method demanded high radiation of roof and floor rock. Sun and Su used the digital image analysis technique to propose a coal-rock interface detection method [6], but it was difficult to obtain a coal-rock image of high quality. Wang and Ding adopted GPR to detect the coal-rock interface by measuring the thickness of the coal seam [7], but the detection depth was seriously limited for complicated geological conditions. A method of multi-sensor data mining and fusion technique in the coal-rock interface recognition system was designed by Ren et al.; however, its installation and use was complicated [8].

The above-mentioned methods focused mainly on differences in hardness, visual, vibration, and other physical characteristics of coal and rock to realize coal-rock identification [9]. In this paper, we are inspired to solve the problem of coal-rock recognition (the cutting state of the shearer) by ESR.

Recently, ESR has been extensively used in coal mines [10]. In the field of coal spontaneous combustion, the free radical reaction characteristics of different coal types were studied using ESR [11]. Feng et al. put forward that free radical concentration could be used as the prediction index of coal seam gas outburst danger [12]. The electron spin resonance (ESR) spectrum parameters were closely related to the degree of coal metamorphism and oxygen content [13]. Qin et al. have studied the change of the coal free radical and revealed that the coal optical property was one of the markers in the tectonic geology of the coalfield [14]. The existing researches mostly focused on the generation mechanisms of the free radical, transfer, and stabilization during the process of coal pyrolysis processing. However, the characteristics of the free radical in the process of different ranks and particle coal/rock samples and coal-rock recognition were rarely involved [15, 16].

In this study, different raw coals/rocks were prepared as the cutting medium and determined by the ESR technique. The physical properties of coals/rocks such as the Landé factor g, line width ΔH, and the concentration of the free radical Ng in the X-band ESR were studied. The statistical classifier method of support-vector machine is employed to build a classification model with the input of the parameters of the ESR absorption spectra.

Experimental. *Instrument.* A micro-ESR spectrometer (Active Spectrum Inc., Foster City, CA) is used to test the ESR parameters, with a magnetic modulation of 100 kHz; the ESR spectra are obtained with high attenuation, a microwave frequency of 9.7 GHz, and a microwave power of 1 mW to avoid signal saturation; the central magnetic field is 3480 G, scanning width 300 G, mod coil amplitude 100%, time constant 5 ms, scanning time 30 s, digital gain 12 dB, number of scans 3, and number of points 4096. The experiments are carried out at room temperature (18–22°C) [17].

ESR Spectroscopy. The most important parameters of the ESR spectrum include the Landé factor g, the concentration of the free radical Ng, and line width ΔH. The Landé factor g characterizes the internal structure of the molecule, the g factor determines the position of the coal sample in the ESR spectrum, the g value of the coal sample is measured with the double comparing method, and the Mn^{2+} is used as the standard sample; after calibrating the g factor, the line width can be read directly from the spectrogram.

It should be noted that in this paper the free radical concentration of the coal sample is determined by the known concentration of the Tempol standard. Meanwhile, the ESR spectra of the coal samples and the Tempol are tested under the same conditions [18, 19].

Experimental samples and the free radical test procedures. In this study, for the ESR measurement we prepare eight different ranks of coal and two different kinds of sandstone, widely used in China. Ten different ranks of coal/rock are investigated, including anthracite of Ningxia Rujigou Mine (RJG), lean coal of Xingtai Xiandewang Mine (XDW), coking coal of Huaibei Daihe Mine (DH), 1/3 coking coal of Xingtai Dongpang Mine (DP), gas fat coal of Xingtai Xingdong Mine (XD), noncaking coal of Kailuan Shanhou Mine (SH), long flame coal of Inner Mongolia Heidaigou Mine (HDG), lignite of Inner Mongolia Shengli Mine (SL), medium sandstone of Yanzhou Xinglongzhuang (XLZ), and silty sandstone of Kailuan Mine (KL).

The details of the sample properties, parts of their proximate analysis, and X-ray fluorescence (XRF) analysis are shown in Table 1.

TABLE 1.The Properties, Proximate, and XRF Analysis of the Coal/rock Samples

No.	Coal samples	Category	Proximate analysis			XRF analysis			
			Volatile	Ash	Al_2O_3	SiO_2	S	P	Matrix
A1	RJG	Anthracite	17.86	13.7	3.58	4.32	0.214	0.01	86.20
B1	XDW	Lean coal	18.47	38.99	7.46	13.05	0.482	0.027	75.90
B2	DH	Coking coal	25.27	41.75	15.62	21.44	0.662	0.01	59.8
B3	DP	1/3 Coking coal	32.81	34.62	5.27	7.04	0.628	0.01	85.5
B4	XD	Gas fat coal	38.56	28.21	3.78	4.00	0.642	0.09	83.00
B4	SH	Non-caking coal	33.89	35.62	3.85	6.26	0.229	0.15	85.10
B6	HDG	Long flame coal	37.59	45.29	20.48	17.67	0.314	0.08	56.50
L1	SL	Lignite	43.13	19.72	22.56	18.24	0.842	0.03	54.61
R1	XLZ	Medium sandstone	–	–	20.32	58.59	0.04	0.06	9.77
R2	KL	Silty sandstone	–	–	21.64	62.9	0.06	0.08	6.97

The categories of coals are sorted according to the classification standard of China coal and ordered by their rank. Volatile matter includes various gas products (H_2, CO, CO_2, etc.) when coal is heated to a certain temperature. The coal ash constituent is the rest of the residue after complete combustion, such as SiO_2, AL_2O_3, and Fe_2O_3. The matrix refers to the components of coal/rock other than the elements in the XRF analysis, such as C, H, and N.

The bulk raw coals/rocks collected from different places are ground into powder with a size from 0.074 to 0.42 mm. Unlike our previous work [20], fresh coal/rock samples are obtained from the center of bulk raw coals/rocks and placed in a grinder for automatic crushing for 2 min; then we screen out the different particle size coals/rocks (instead of the powder pressed into tablets), and the coals/rocks are placed into 5 mm quartz ESR tubes and then sealed. In order to decrease the measurement error, each sample is tested three times and then the results are averaged. The experimental procedure includes the following:

1. Ten kinds of coal/rock samples with different particle sizes, ~1–40 mesh (0.42–1.00 mm), ~40–80 mesh (0.18–0.42 mm), ~80–120 mesh (0.125–0.180 mm), ~120–160 mesh (0.100–0.125 mm), and ~160–200 mesh (0.074–0.100 mm), are tested.

2. Preparing 100 sets of coal/rock samples (~160–200 mesh (0.074–0.100 mm)) and then measuring each kind of the sample. We obtain a data set of 100 ESR spectra. Then the method of SVM is employed to build a model to classify the coal/rock.

Mathematical methods. Support vector machine (SVM) is a statistical classification method based on the structural risk minimization approach proposed by Vapnik et al. [21]. The basic principle of SVM is that it can find the optimal separating hyperplane that minimizes the upper bound of the generalization error by maximizing the margin between the separating hyperplane and the nearest sample points. For the nonlinear classification, the input sample space is mapped to a high dimensional feature space through a nonlinear mapping method (Kernel), and the nonlinear classification of the sample space is transformed into the linear classification. For the linear 2 class classification, the separation hyperplane has to satisfy the following:

$$w^T x + b = 0, \tag{1}$$

where w is the normal vector and b is the bias term. The classification of data set X_i depends on the decision function:

$$f(x) = \mathrm{sign}(w^T x_i + b). \tag{2}$$

For the k class classification, the one-versus-one method is usually employed.

Results and discussion. *The ESR spectra and free radical characteristics of coals and rocks.* Coal consists of a variety solid, combustible, sedimentary, organic rocks formed over millions of years. The complexity of the coal molecular structure and the diversity of its functional groups result in the complexity and diversity of the free radical in coal and rock. The measured free radical concentration is actually a mixture spectrum of the free radical. In this section, the spin resonance properties of ten kinds of metamorphic grade coal/rock samples are tested under different crushing degrees; the samples spectra are presented in Fig. 1. As can be seen, with increase in the fragmentation degree, the intensity of all the ESR spectra displays an increasing tendency, and with increase in the coals/rocks rank, the intensity of all the ESR spectra also grows.

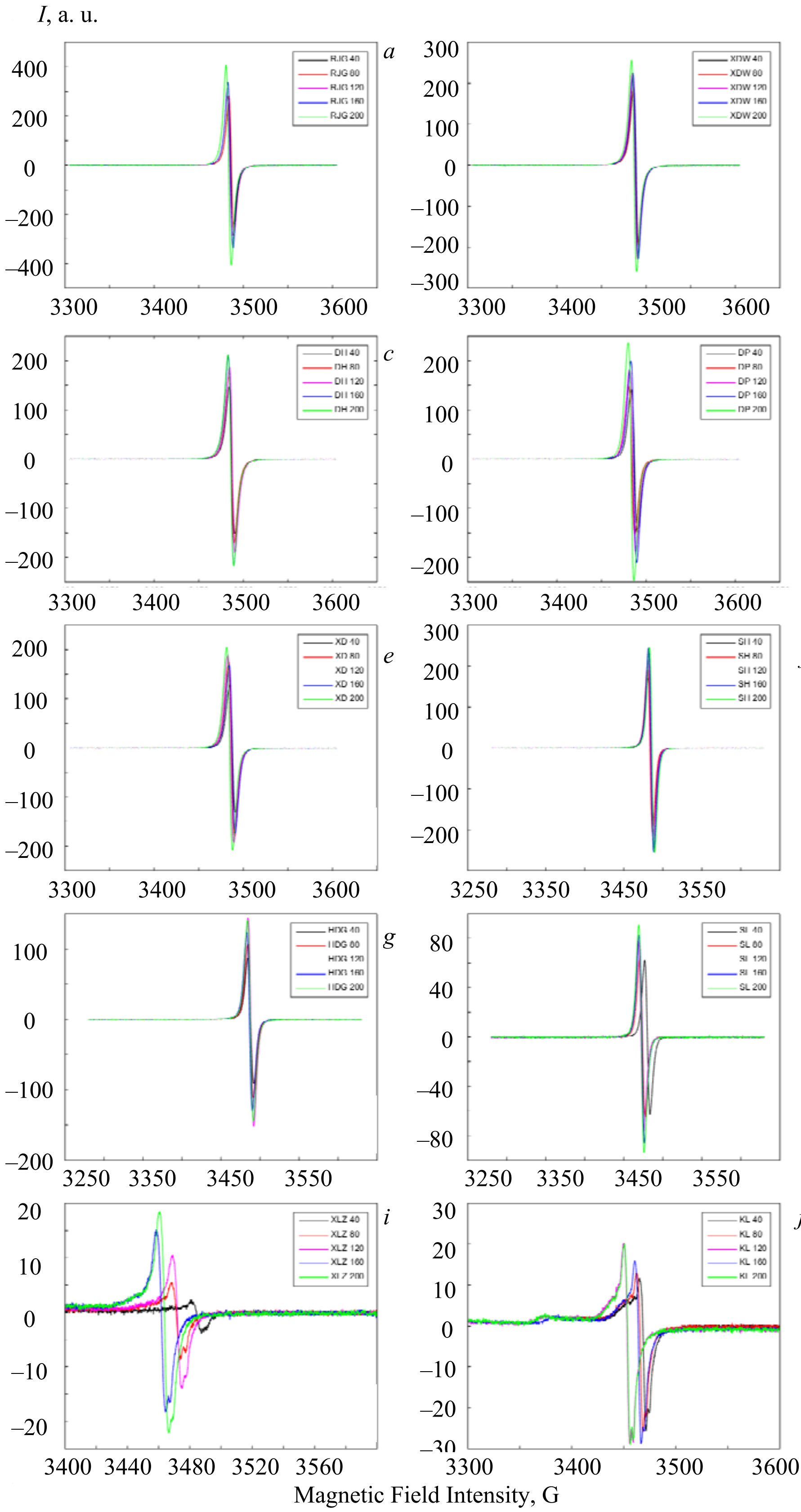

Fig. 1. The ESR spectra of different coals/rocks sample: (a) RJG coal, (b) XDW coal, (c) DH coal, (d) DP coal, (e) XD coal, (f) SH coal, (g) HDG coal, (h) SL coal, (i) XLZ rock, (j) KL rock, microwave power 1 mW.

The variation of the g factor with different particle sizes is shown in Fig. 2. The g factor of ten groups of the coals/rocks free radical is between 2.002 and 2.003; the unpaired electrons of coal free radicals are localized in the C, O, N, S, and P atoms; and the unpaired electrons of the rock free radical mainly include metal oxide oxygen defects, silicate material hanging keys, defects, etc. The g factor value decreases with increase in coal rank. In particular, the g value of two kinds of sandstone is less than that of lignite but greater than other bituminous coal and anthracite; the change in the g value is related to the free radical species and the impurity atoms.

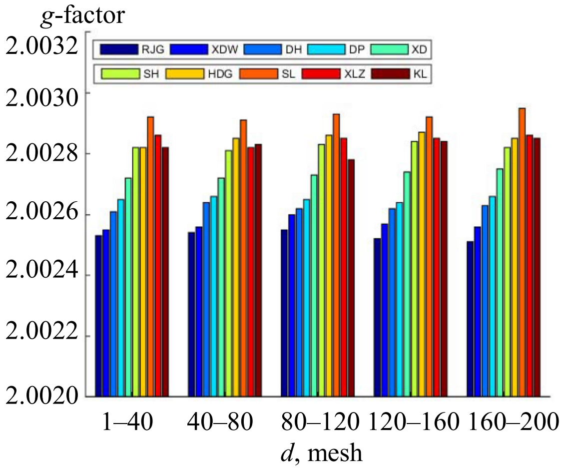

Fig. 2. The variation of g factor with the particle size d.

Petrakis et al. have collected the g value of some free radicals; the value of the free radical containing nitrogen is 2.0031, and the free radical containing sulfur ranged from 2.0080 to 2.0081 [22]. The coal with a lower rank has more free radicals of the oxygen functional groups. The impurities in coal such as nitrogen and sulfur have a greater impact on the g value, so the SL coal sample g value is larger. Anthracite has less impurity atoms, and the aromatic free radical and alkyl radical are higher than the gas coal and fat coal. Therefore, the g factor value of RJG is small.

The variation of the line width with different particle sizes is shown in Fig. 3a. The line width of the eight groups of metamorphic grade coal varies with the degree of fragmentation, as is shown in Fig. 3a; the line width value of five kinds of bituminous coal show little difference, except for HDG bituminous. However, they are significantly higher than for anthracite. From the coal species, because XDW, DH, DP, XD, and SH are five groups of bituminous coal, the coal sample width shows little difference. But the line width of HDG is singularly higher. On the contrary, the line width of RJG is significantly lower. Therefore, in addition to HDG, the following relationships between the line width of different kinds of metamorphic grade coal exist: lignite > bituminous coal> anthracite. With increasing coal rank, the line width of the free radical becomes narrower. For two kinds of sandstone, the change in the line width is small but higher than for RJG and XDW and lower than for DH.

The variation of the free radical concentration with different particle sizes is shown in Fig. 3b. The free radical concentration of RJG is significantly higher than that of the low metamorphic grade coal samples, and the free radical concentration of anthracite is the largest. The free radical concentrations of eight kinds of metamorphic grade coals and two kinds of rock samples increase with increasing degree of fragmentation, except for the free radical concentrations of XDW, XD, HDG, and KL, whose particle sizes are 0.18–0.42, 0.42–1.00, 0.074–0.100, and 0.100–0.125 mm, respectively. A comparison of the free radical concentration between the maximum and minimum granules is shown in Table 2. As can be seen from Table 2, the maximum value of the free radical concentration is found in the smallest-particle coal. During the process of coal low-temperature oxidation, the particle size of coal changes, and the free radical concentration changes significantly. In other words, the fragmentation process can produce new free radical reactions. Furthermore, there are significant differences in the free radical characteristics for different ranks of coals and rocks. With increasing the coal/rock rank, the concentration of the free radical grows. In other words, with increasing carbonization degree, the concentration of the free radical also increases. Therefore, the degree of carbonization is also an important factor for the free radical concentration of coal/rock samples. It should be noted that in the future more meaningful physical characteristics will be studied [23–26]. So, ESR spectroscopy has proved that coal and rock have different free radical characteristics. Thus, we can use an estimation of the free radical characteristics of coal and rock combined with the mathematical method to design a new method for the classification of coal and rock.

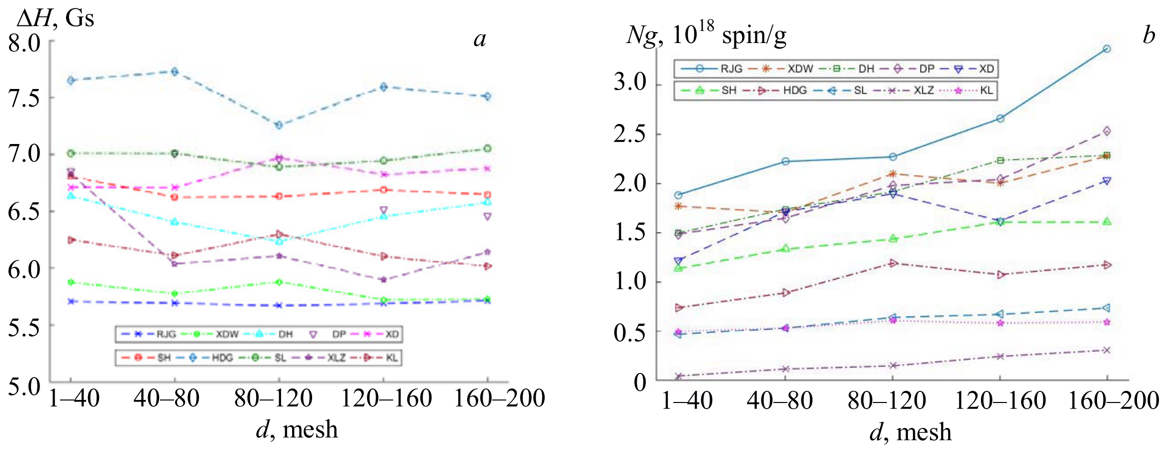

Fig. 3. The change in line width (a) and free radical concentration (b) with particle size.

TABLE 2. Comparison of Free Radical Concentration (mas.%) between the Maximum and Minimum Granules

Coal samples	RJG	XDW	DH	DP	XD	SH	HDG	SL	XLZ	KL
Maximum particle	1.89	1.77	1.50	1.48	1.22	1.13	0.74	0.46	0.06	0.49
Minimum particle	3.37	2.28	2.28	2.53	2.03	1.61	1.17	0.73	0.30	0.59
Increment of free radical concentration	1.48	0.51	0.78	1.05	0.81	0.48	0.43	0.27	0.24	0.10
Growth rate of free radical concentration, %	78	29	52	71	66	42	58	59	500	20

Classification of coals and rocks. The discussion above indicates that the characteristics of different coals/rocks in the X-band ESR are variable. In order to build a robust and precise model, a statistical method, SVM, is used. The scheme of the classification model is presented in Fig. 4.

In our study, we prepare 100 sets of coal/rock samples (~160–200 mesh (0.074–0.100 mm)), measure each kind of sample, and get a total data set of 100 ESR spectra, and the *g* factor, line width, and free radical concentration of the coal/rock samples are applied as the feature data set, which has 100 rows and 3 columns, divided into the training set and the test set. As is shown in Fig. 4, before SVM training and prediction, the data normalization preprocessing is carried out. Then the method of SVM is employed to build a model to classify the coal/rock. As mentioned above, the data set is randomly divided into the training set (40 coal samples, 10 rock samples; 50 in total) and the test set (40 coal samples, 10 rock samples; 50 in total). The cross validation is used in the model building process, and the classification accuracy of the training set and the test set are 100%.

Meanwhile, in Fig. 5a, the test result with a 100% classification accuracy indicates that the ESR-SVM model is robust and precise and the proposed method can be used for coal-rock interface detection. Furthermore, the data are divided into four categories, as mentioned above: anthracite coals (5 training samples and 5 test samples), bituminous coals (30 training samples and 30 test samples), lignite coals (5 training samples and 5 test samples), and rocks (10 training samples and 10 test samples). As is shown in Fig. 5b, the classification accuracy of the training set is 100%, and the same for the test set, by using the coals/rocks ESR spectra data.

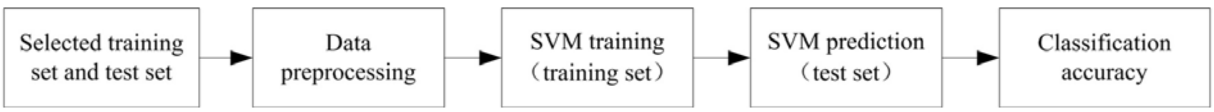

Fig. 4. The construction of the classification model.

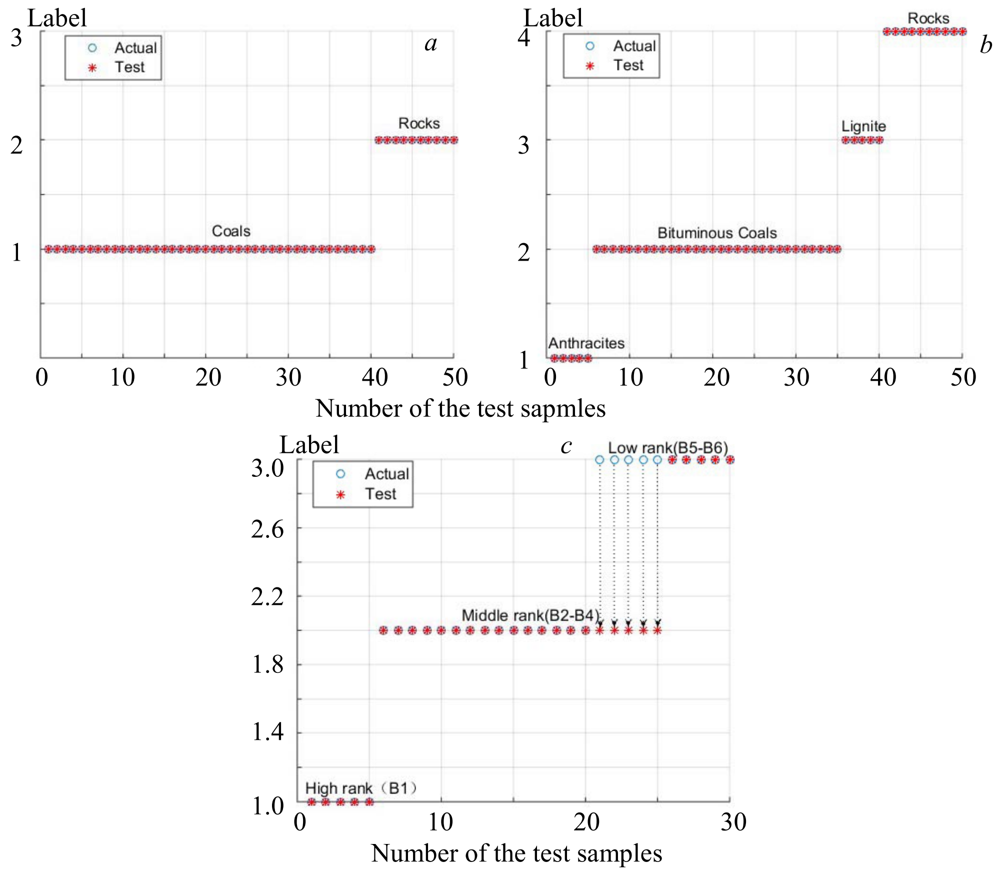

Fig. 5. The classification result of coal and rock (a), different ranks of coals and rocks (b), different ranks of bituminous coals (c).

In addition, the data of bituminous coals (XDW, DH, DP, XD, SH, and HDG) are divided into three categories: high-rank bituminous coals (5 training samples and 5 test samples), middle-rank bituminous coals (15 training samples and 15 test samples), low-rank bituminous coals (5 training samples and 5 test samples). As is shown in Fig. 5c, the classification accuracy of the training set is 93.3% and that of the test set is 83.3% using the coals/rocks ESR spectra data. The result of the ESR absorption spectra demonstrates a better performance for the ESR-SVM model. The ESR-SVM method can be a promising tool for the classification of different coals.

As can be seen from Table 3, the parameters, accuracy, and operation speed of the classification model can be calculated. By selecting the best parameters, the classification accuracy of coal and rock samples can be 100%, and the classification processing time is 5.3 and 7.1 ms. But the classification accuracy of bituminous is not very good, 93.3% (train set) and 83.3% (test set), the classification processing time is 6.8 ms.

TABLE 3. Parameters and Recognition Results of the ESR-SVM Model

Data set	Categories	*c*	*g*	Train set	Test set	Time, ms
Coal/Rock	2	2	7	100% (50/50)	100% (50/50)	5.3
Coal/Rock	4	4	9	100% (50/50)	100% (50/50)	7.1
Bituminous coal	3	2	1	93.3% (28/30)	83.3% (25/30)	6.8

Conclusion. We look forward to solving the coal/rock recognition by ESR. In our paper, we studied eight kinds of coal and two kinds of sandstone, very common in China's coal mining and difficult for recognizing by other coal-rock detection methods, such as the gamma ray method. The physical properties of coals/rocks using ESR are established, and the different responses caused by diverse components in coals/rocks indicate that the different samples can be classified by the ESR technique. As a result, a model is established for recognizing coals/rocks using the mathematical SVM method with the free radical characteristics of coals/rocks. The proposed ESR-SVM method has a recognition rate of 100% for coals/rocks. The study reveals that the proposed method is fast, stable, and accurate for the detection of the coal-rock interface.

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