Pore Fractal Characteristics of Suancigou Long-Flame Coal after Electrochemical Treatment: An Experimental Study through the Implementation of N₂ Adsorption and Mercury Intrusion Prosimetry Techniques

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ABSTRACT: The application of electrochemical treatment in coal seams for enhancing coalbed methane (CBM) recovery can also decrease the risks of outburst disasters. The long-flame coal samples were electrochemically modified with 0, 1, 2, and 4 V/cm electric potential gradients, and the pore structures were measured and analyzed by combined low-temperature nitrogen gas adsorption, mercury intrusion prosimetry, and fractal theory. The experimental test results indicated that the pore volumes of macropores (>50 nm) and mesopores (2–50 nm) increased after electrochemical modification and further increased with the increase in electric potential gradient. The fractal dimensions of pores showed a decreasing trend except for the slight fluctuation of the mesopores with a size of 2–4.5 nm after modification, which indicated that the overall roughness and irregularity index of pores decreased. The evolution mechanisms of pore size distributions and their fractal dimensions were explained by the dissolution of minerals and the falling off of alkane side chains in the coal surface, which would expand and connect the pores during the electrochemical modification process. The results obtained from this work were crucial for CBM exploration via an electrochemical method.

1. INTRODUCTION
The exploration and development of coalbed methane (CBM) have attracted global attention for the utilization of clean energy.1–3 Given that the gas is stored in the coal inner surface with complicated pore structures, it is of great significance to optimize pore structures and have a better understanding of the relationship between gas adsorption and pore characteristics. Physical and chemical modifications used for the optimization of coal pore structures have been reported such as microwave irradiation modification,4–6 acid modification,7 alkali modification,8,9 and electrochemical modification.10,11

For accelerating CBM recovery, the pore structures of lignite, sub-bituminous, bituminous, and anthracite were tested by nuclear magnetic resonance (NMR) after irradiation modification by Li et al.4 Also, the results showed that all the pore size distributions of coal samples were extended, and the pore volume and pore connectivity increased after irradiation modification. After acid modification with H₂SO₄ and (NH₄)₂S₂O₈, the surface area and pore volume of bituminous coal increased due to the connection of closed pores, while the average pore diameter decreased.7 The supermicropores (0.7–2 nm) of anthracite samples were increased by NaOH activation.8 The ratios of micropores (<2 nm) and mesopores (2–50 nm) of anthracite samples were significantly increased after NaOH modification.7 The fractures of about 91.2 μm of anthracite samples increased after electrochemical modification due to the removal of minerals that filled the fractures; as a result, the gas diffusion distance and desorption time were shortened.10 The advantages of electrochemical modification fused the controllability of the directions of coal particles and water, uniform distribution of electroosmotic flow, and insensitivity to the pore size.12,13

The fractal theory combined with LP-N₂GA tests, NMR tests, mercury intrusion prosimetry (MIP) tests, focused-ion beam-scanning electron microscopy (FIB-SEM), and X-ray computed micro-tomography (X-ray μ-CT) is a good method for characterizing the pore structures of coal and other porous materials.
Su et al. discussed the effect of modification on the fractal dimensions of pore structures of long-flame coal, and the results showed a continuously decreasing tendency after cyclical supercritical CO₂ treatment. Zhao et al. reported a mathematical framework that can characterize the fractal pore structure via combined MIP, N₂ adsorption tests, and fractal theory to characterize selected coals in China. Different from the research studies that defined a coal matrix as “dual-porosity” of Zhao et al. and Barenblatt et al., Niu et al. reported the fractal dimensions of adsorption pores by liquid nitrogen adsorption, small angle X-ray scattering (SAXS), and scanning electron microscopy (SEM). Niu et al. found that the fractal dimensions increase with the increase in metamorphism degrees of coal samples, and increased speed is
controlled by the pore structure, macromolecular structure, and surface morphology of pores in coals. In addition, Xiao et al. reported an analytical fractal model where every parameter has a clear physical meaning. Guo reported that the fractal dimensions of micropores and macropores of anthracite all decreased significantly after electrochemical modification. Thus, the fractal theory is an important and effective method to characterize the effect of electrochemistry on coal pore structures.

However, research studies about the effects of the electrochemical modification on pore structures and fractal dimensions of long-flame coal were limited. In this work, we electrochemically modified long-flame coal samples with 0, 1, 2, and 4 V/cm electric potential gradients. The pore structures and alkane side chains of long-flame coal samples before and after modification were tested by LT-N2GA, MIP, and Fourier transform infrared (FTIR) spectrum techniques. The pores were reclassified into four zones according to their complexity degrees, which was reasonable to characterize the pore structures of electrochemically modified long-flame coal. Also, the mechanism of electrochemical modification was further explained by fractal characteristics of the modified long-flame coal.

2. RESULTS AND DISCUSSION

2.1. LT-N2GA Analysis. 2.1.1. N2 Isothermal Adsorption/Desorption Curves. Figure 1 shows the N2 adsorption/desorption isotherms of long-flame coal samples before and after electrochemical modification with different potential gradients. The adsorption isotherms illustrated that long-flame coal samples are rich in micropores, mesopores, and macropores. The N2 adsorption in long-flame coal was reversible physical adsorption, and the isotherms all belonged to IV-type curves. N2 adsorption turned from monolayer adsorption \( (p/p_0 < 0.2) \) to multilayer adsorption \( (p/p_0 > 0.2) \), and even capillary condensation appeared. All the hysteresis loops were H4-type curves when the relative pressure was approximately greater than 0.4, indicating that a large number of slit pores existed in the samples. After electrochemical modification, the changes in morphology generated by the adsorption−desorption hysteretic loops are limited, while the amount of adsorbed N2 is higher than that of unmodified long-flame coal samples. It means that the electrochemical modification mainly increases the number of pores and has limited influence on the pore morphology. After electrochemical modification with potential gradients of 1, 2, and 4 V/cm.

### Table 1. Pore Surface Areas of Long-Flame Coal Samples before and after Electrochemical Modification

| samples | surface area (m²/g) |
|---------|---------------------|
| 0 V/cm  | 3.52 0.07           |
| 1 V/cm  | 3.53 0.09           |
| 2 V/cm  | 3.57 0.10           |
| 4 V/cm  | 3.61 0.09           |

Figure 3. (a) Results of FTIR spectrum tests after electrochemical modification with 0, 1, 2, and 4 V/cm and the enlarged view of (b) −CH₂ and −CH₃ and (c) minerals.
V/m, the amount of adsorbed N₂ increased from 19.23 cm³/g to 22.79, 27.81, and 28.98 cm³/g with increments of 3.56, 8.58, and 9.75 cm³/g, respectively, which indicates that more pores were generated at high potential gradients.

2.1.2. BJH Pore Size Distribution. Figure 2 shows the pore size distribution (PSD) of long-flame coal samples before and after electrochemical modification. Compared with the raw samples, the PSDs of the modified samples were not changed obviously different. After electrochemical modification, the differential pore volume (dV/dP) and cumulated pore volume of long-flame coal samples increased when the pore size was larger than 2 nm. The cumulative pore volume of long-flame coal samples increased with the increase in potential gradients; this was consistent with the results of Figure 1 and the investigation of Guo et al.10

Figure 4. Relationship between ln(V) and ln(ln(Po/P)) based on long-flame coal samples LP-N₂GA data after electrochemical modification with (a) 0, (b) 1, (c) 2, and (d) 4 V/cm and fractal dimensions (e).

Figure 5. Mercury intrusion–extrusion curves of long-flame coal samples before and after electrochemical modification. In: intrusion; Ex: extrusion.

Figure 6. Pore size distribution of long-flame coal samples before and after electrochemical modification.
After electrochemical modification with potential gradients of 1, 2, and 4 V/m, the pore volume from 0.0359 cm³/g increased to 0.0426, 0.0498, and 0.0523 cm³/g with increments of 0.0067, 0.0139, and 0.0164 cm³/g, respectively. The reason was that some low molecular weight compounds such as short chain alkanes in the macromolecular structure of coal can be removed, resulting in the increase in pore volume.²⁸,²⁹ Some minerals such as calcite, dolomite, and magnesite could be dissolved by the H⁺ species generated in the anode zone.³⁰

Figure 3 shows the FTIR spectrum test results of raw coal samples and modified coal samples. It can be seen that the peaks in the region of wavenumbers 2800−3000 cm⁻¹ correspond to the vibrations of alkane side chains (such as methyl and methylene) in a coal macromolecular structure, and the peak near the 1445 cm⁻¹ wavenumber was attributed to the vibration of minerals (such as carbonate). After electrochemical modification, some of the methyls and methylenes were broken and fell off from the macromolecular structure of coal, resulting in the reduction of alkane side chains (Figure 3b). Simultaneously, the H⁺ species produced by electrochemical reactions dissolved some carbonate, resulting in the reduction of minerals (Figure 3c). The above phenomena in the process of electrochemical modification would promote the expansion and connectivity of pores. In addition, the coal matrix will swell or shrink due to a temperature change during the process of electrochemical modification, causing the fatigue damage of the coal matrix and the formation of new pores. Zhang et al.²⁴ found that some organic and inorganic substances usually embedded in the surface of pores or filled the throat between pores. This explanation is confirmed by the pore expansion in electrochemical modification experiments.

The increase in the surface area for the pores >2 nm indicates that some mesopores expanded during the electrochemical modification process, as shown in Table 1. Considering that the amount of methane molecules adsorbed in the inner surface of pores is constant, the increase in pores results in a methane movement increase, which will promote methane extraction in coal seams.

2.1.3. FHH Fractal Dimensions. The pore fractal dimensions of long-flame coal can be effectively reflected by the Frenkel–Halsey–Hill (FHH) model, and the formula for calculations is as follows:³¹

\[
\ln \left( \frac{V}{V_0} \right) = A \ln \left( \frac{P}{P_0} \right) + C_1
\]

That is

\[
\ln(V) = A \ln \left( \frac{P}{P_0} \right) + C_2
\]

where \(V_0\) is the volume of adsorbed N\(_2\) at the pressure of \(P_0\) cm\(^3\)/g; \(V\) is the volume of \(N_2\) in the monolayer, cm\(^3\)/g; \(P_0\) is the saturated \(N_2\) pressure, MPa; \(A\) is the slope of the double logarithmic curve drawn by \(\ln(V)\) to \(\ln(\frac{P}{P_0})\); and \(C_1\) and \(C_2\) are constants, dimensionless. The fractal dimension \(D\) can be obtained from eq 2:³²

\[
D = A + 3
\]

The FHH fractal curves can be divided into two sections with \(P/P_0 = 0.5\) as the dividing point. For \(P/P_0 < 0.5\), the fractal dimension \(D_1\) can be used to represent the surface roughness of mesopores (2−50 nm). Conversely, for the stage of \(P/P_0 > 0.5\), the dimension \(D_2\) can be used to express the irregularity degree of mesopore structures.

Figure 4 shows the fitting results of fractal dimensions of long-flame coal samples before and after modification. The values of \(D_1\) (2.0147−2.0644) and \(D_2\) (2.8989−2.9366) were all between 2 and 3, showing that the pores in all samples had good fractal characteristics.³³ After 1, 2, and 4 V/cm
 electrochemical modification, the $D_2$ gradually decreased from 2.9366 to 2.9126, 2.9027, and 2.8989, respectively, and the descending rate also decreased, indicating that the irregularity degree of mesopores decreased. The reason was that the expansion and connection made the arrangement of pores simpler. However, the changing law of $D_1$ is different from that of $D_2$. It continued to decrease after 1 and 2 V/cm modification but began to increase after 4 V/cm modification, showing that the surface roughness of mesopores decreased first and then increased. The reason was that some alkane side chains in a coal macromolecular structure were broken and removed with electrochemical modification, making the surface of pores smoother. Contrarily, the heterogeneous corrosion of minerals that filled the pores made the surface of pores more uneven. As a result, the surface roughness of mesopores decreased first and then increased, which were consistent with the results of Guo.\textsuperscript{23}

2.2. MIP Analysis. 2.2.1. Mercury Intrusion–Extrusion Curves. Figure 5 shows the mercury intrusion–extrusion curves of long-flame coal samples before and after modification. It can be seen that the maximum mercury input of raw samples was 0.33 cm$^3$/g, increasing to 0.57, 0.64, and 0.79 cm$^3$/g after 1, 2, and 4 V/cm electrochemical modification, respectively, increasing by 70.51, 93.40, and 137.99%. The results indicate that the total volume of the pores increased continuously with the increase in the potential gradient during modification.

2.2.2. Pore Size Distribution of MIP. Figure 6 shows the PSD curves of coal samples before and after modification. It can be seen that MIP can measure the pores in a wide range, but it might not be so accurate for the pores with a small size (<50 nm). There were several peaks that mainly contributed to the PSD curves. The peaks in the range of $2-4 \times 10^4$ and around $1 \times 10^5$ nm increased remarkably, indicating that some pores or cracks were widened or opened. The reason was that the H$^+$ ions generated in the anode zone during the electrochemical modification process would dissolve some carbonate minerals such as calcite, siderite, and aragonite that filled the cracks of coal samples. Part of clay minerals such as kaolinite and montmorillonite also would be dissolved by the OH$^-$ species generated in the cathode zone.

Figure 7 shows the cumulative volume and specific surface area of pores. It can be seen that the cumulative pore volume increased continuously with the increase in electric potential gradient, while the cumulative pore area increased first, then decreased slightly, and then increased. As the electric potential
gradient increased, the number and size of pores increased gradually, resulting in the increase in cumulative pore volume and surface area. It should be noted that when the potential gradient was 2 V/cm, the surface area decreased slightly due to the connectivity of some pores. The surface area was almost contributed by the pores smaller than 100 nm. On the contrary, except for pores below 100 nm, which contribute a small part of the volume, most of the volume is provided by pores above 10 μm.

2.2.3. Menger Fractal Dimensions of MIP. The Menger sponge model is suitable for calculating the fractal dimension $D$ of pores based on mercury injection tests.\textsuperscript{31,34,35} According to the Washburn equation, the radius $r$ of pores that are filled with mercury at pressure $P_M$ is expressed as\textsuperscript{36}

$$ P_M = \frac{2\sigma \cos \theta}{r} $$

(4)

where $\sigma$ is the surface tension of mercury (0.48 N/m) and $\theta$ is the mercury—coal contact angle (130°). The relationship between pore size distribution $dV_M/dr$ and the fractal dimension $D$ is\textsuperscript{37}

$$ \frac{dV_M}{dr} \propto r^{2-D} $$

(5)

Combining eqs 4 and 5, we get

$$ \frac{dV_M}{dP_M} \propto P_M^{D-4} $$

(6)

That is

$$ \log \left( \frac{dV_M}{dP_M} \right) \propto (D-4)\log P_M $$

(7)

where $V_M$ is the volume of cumulative injection mercury, which is approximated by the pore volume, cm$^3$/g; $P_M$ is the pressure of mercury injection, MPa; and $r$ is the radius of pores, μm.

Figure 8 shows the fractal dimension curves of long-flame coal samples using the Menger sponge model. It can be seen that all the curves were divided into three segments. Except for the zone with a pore size less than 50 nm, the other two segments had strong fractal characteristics. The reason was that although the pores with a wide range can be measured by MIP, there were still limitations on the lower testing accuracy of the smaller pores (<50 nm). Therefore, the pores with a size greater than 50 nm were analyzed based on MIP. The fractal dimensions of the two segments of raw samples were 2.7140 and 2.4567, respectively, and the corresponding pore ranges are 50–20,000 nm and >20,000 nm, respectively. After electrochemical modification, $D_3$ and $D_4$ continuously decreased to 2.4562 and 2.1718, respectively, indicating that the order index of pores increased.

2.3. Pore Classification and Analysis. The comprehensive fractal method by FHH combined with Menger fractal dimensions was introduced to diminish the measurement error of LP-N$_2$GA and MIP in analyzing the pores of long-flame coal samples before and after electrochemical modification, as shown in Figure 9. It can be seen that the pores before and after modification had strong piecewise fractal characteristics. The total pores can be divided into four ranges: Z1, 2–4.5 nm, corresponding to $D_1$; Z2, 4.5–50 nm, corresponding to $D_2$; Z3, 50–20,000 nm, corresponding to $D_3$; and Z4, >20,000 nm, corresponding to $D_4$.

Table 2 shows the pore volume in the zones of Z1–Z4 and their proportions. It can be seen that although the volume of micropores and mesopores increased, their proportions decreased. The main reason was the sharp increase of macropores, especially the volume of fractures (Z4 zone). The fractures with a width greater than 20 μm contributed most of the total pore space. After 4 V/cm electrochemical modification, the volume of fractures in Z4 increased from...
Based on the value of \( R \) the long-flame coal samples were a low metamorphosed bituminous coal. Following the China National Standards of GB/T 212-2008, GB/T 476-2008, and GB/T 2142007, the proximate analysis and element analysis results of long-flame coal samples were obtained, as listed in Table 3. The coal samples were processed into fine particles of 0.18–0.25 mm according to GB/T 19560-2004 for tests.

4. EXPERIMENTS

4.1. Coal Samples. The long-flame coal samples were collected in the Suancigou mine of Inner Mongolia Yitai Group, China. The maximum vitrinite reflectance \( (R_{o,max}) \) of the long-flame coal samples was determined via an Axioskop 40A reflective polarizing microscope (manufactured by Zeiss Instruments, Germany). Based on the value of \( R_{o,max} \) (0.7129%) and GB5751-1986, the long-flame coal samples were a low metamorphosed bituminous coal. Following the China National Standards of GB/T 212-2008, GB/T 476-2008, and GB/T 2142007, the proximate analysis and element analysis results of long-flame coal samples were obtained, as listed in Table 3. The coal samples were processed into fine particles of 0.18–0.25 mm according to GB/T 19560-2004 for tests.

4.2. Experimental Apparatus. The prepared long-flame coal samples were modified in the apparatus shown in Figure 10. The apparatus for modification is mainly composed of an adjustable direct current (DC) power supply, an electrolyzer, two electrode plates, and several connecting wires. The long-flame coal samples and the \( \text{Na}_2\text{SO}_4 \) electrolyte with a concentration of 0.05 mol/L were placed in the electrolyzer with a size of 250 mm long, 180 mm wide, and 100 mm high.\(^{38,39}\) The DC power supply with an output voltage of 0–110 V and output current of 0–3 A was a DH1722A-2 produced by Dahua Radio Instrument Factory. The electrolyzer was made of acrylic to avoid chemical reactions with the electrolyte, acid, or alkali. Two graphite electrode plates with a size of 150 × 100 × 5 mm were connected with the anode and cathode.

4.3. Experimental Process. The long-flame coal samples were treated in four different potential gradients (electric field intensities). The coal sample immersed in the \( \text{Na}_2\text{SO}_4 \) electrolyte without the applied electric field was denoted by T1. The samples modified in the \( \text{Na}_2\text{SO}_4 \) electrolyte with the electric field intensities of 1, 2, and 4 V/cm were denoted as T2, T3, and T4, respectively. The coal samples were previously tested and analyzed in our further research.

![Figure 10. Schematic diagram of the electrochemical modification apparatus.](image)

### Table 2. Pore Volumes in Different Zones and Their Proportions

| Samples | Parameter | \(2\sim4.5\) nm | \(4.5\sim50\) nm | \(50\sim20,000\) nm | >20,000 nm |
|---------|-----------|-----------------|-----------------|---------------------|------------|
| 0 V/cm  | pore volume (cm³/g) | 0.0115 | 0.0171 | 0.0214 | 0.2736 |
|         | percentage, % | 3.55 | 5.28 | 6.61 | 84.55 |
| 1 V/cm  | pore volume (cm³/g) | 0.0134 | 0.0175 | 0.0245 | 0.4992 |
|         | percentage, % | 2.42 | 3.16 | 4.42 | 90.01 |
| 2 V/cm  | pore volume (cm³/g) | 0.0144 | 0.0188 | 0.0313 | 0.5684 |
|         | percentage, % | 2.28 | 2.97 | 4.95 | 89.81 |
| 4 V/cm  | pore volume (cm³/g) | 0.0168 | 0.0192 | 0.0294 | 0.7192 |
|         | percentage, % | 2.14 | 2.45 | 3.75 | 91.66 |

### Table 3. Analysis Results of Anthracite Samples

| Vitrinite | Semi-vitrinite | Intinite | Exinite | Mineral | Moisture | Ash Yield | Volatile Matter | Fixed Carbon | Ultimate Analysis (%) |
|----------|---------------|---------|---------|---------|----------|-----------|-----------------|---------------|------------------------|
| 50.10    | 8.70          | 20.50   | 9.00    | 11.70   | 6.01     | 30.32     | 23.68           | 40.00         | 78.92 5.55 13.62 1.20 0.71 |

0.2736 to 0.7192 cm³/g and its fraction increased from 83.31 to 90.98%, increasing by 162.87 and 9.21%, respectively. The main reason for this phenomenon is the dissolution of minerals that filled the macropores and fractures by the electrochemical actions mentioned above.

### 3. CONCLUSIONS

(1) For electrochemically enhanced CBM extraction, the pore structures and the fractal characteristics of long-flame coal samples before and after modification were characterized by LT-N₂-GA combined with MIP analysis.

(2) With the increase in electric potential gradients, the volume and surface area of micropores decreased, while the volume of mesopores, macropores, and fractures increased. The main reason was the development, expansion, and connection of pores by electrochemistry.

(3) During the modification processes, the fractal dimensions \( D_2, D_3 \) and \( D_4 \) continuously decreased, despite \( D_1 \) fluctuating a little. It indicates that for the total pores, the complexity decreased and the order degree increased due to the change on the surface of coal (removal of some alkane side chains such as \( -\text{CH}_3 \) and \( -\text{CH}_2 \)) and the change in the pore structures (dissolution of some minerals that filled the pores and fractures).

(4) The effect of electrochemical modification on the pore fractal dimensions of Suancigou long-flame coal has been discussed above. There are still issues that need a better understanding by more kinds of test methods and coal samples. Only one test for each long-coal sample was conducted, which will lead to unsound results; and different coal ranks, test means (like CO₂ adsorption and small-angle X-ray/neutron scattering techniques), and more types of electrochemical parameters will be tested and analyzed in our further research.
processed into 60–80 mesh particles and dried to constant weight in a vacuum drying oven at 373.15 K. Dried samples (100 g) were used in each modification experiment lasting for 120 h.

The LT-N, GA and MIP tests are used to characterize the pore structures with the pore size in ranges of 1.7–300 nm and 7.5–11,000 nm by an ASAP 2020HD88 specific surface area measuring instrument and a Pore Master 33 provided by Taiyuan University of Technology.

The FTIR test are used to characterize the change of alkane side chains and removal of minerals by a Nicolet iS5 FTIR instrument.

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